

## **THERMODYNAMIC FUNCTIONS OF GASEOUS LITHIUM, SODIUM, POTASSIUM, RUBIDIUM AND CAESIUM SULFATES**

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### **ABSTRACT**

The free energy functions and entropy of alkali metal sulfates were calculated and are reported in this paper. The IR and Raman spectra of  $\text{Li}_2\text{SO}_4$  were explored in the range  $30\text{--}1200\text{ cm}^{-1}$  while the far IR (below  $600\text{ cm}^{-1}$ ) was investigated for all the other molecules. A theoretical model was employed to estimate the molecular parameters needed in the calculation of the thermodynamic functions.

### **INTRODUCTION**

In the course of recent years, the results of spectroscopic [1–3] and electron diffraction studies [4] have been used almost exclusively for elucidating the molecular geometries of stable inorganic molecules in the vapour phase. In particular, the studies on gaseous sulfates have proved that molecules of the type  $\text{M}_2\text{SO}_4$  have bidentate binding.

Work already published on the alkali metal sulfates does not provide complete data to calculate accurate free energy functions and entropies for these molecules. Electron diffraction data are complete for  $\text{K}_2\text{SO}_4$  and  $\text{Cs}_2\text{SO}_4$  only; spectroscopic studies have been limited, up to now, to the investigation of the vibrational frequencies of the  $\text{SO}_4^{2-}$  group. Nothing is known about the low frequencies of the vibrational modes of the metal with respect to the rest of the molecule. These data are particularly important because the low vibrational frequencies represent an important contribution to the thermodynamic function values. Therefore we extended the IR and Raman investigation of  $\text{Me}_2\text{SO}_4$  type molecules ( $\text{Me} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) to the low frequency range of the IR spectrum. In addition, we employed the results of the electrostatic model to correctly assign the far IR spectra of the molecules and to estimate unobserved frequencies as well as bond distances and angles not available in the literature.

TABLE 1  
 Summary of the experimental and calculated vibrational frequencies ( $\text{cm}^{-1}$ ) of  $D_{2d}$  symmetry alkali sulfates

Symmetry of the vibration	Li <sub>2</sub> SO <sub>4</sub>		Na <sub>2</sub> SO <sub>4</sub>		K <sub>2</sub> SO <sub>4</sub>		Rb <sub>2</sub> SO <sub>4</sub>		Cs <sub>2</sub> SO <sub>4</sub>	
	Calcd.	Exp.	Calcd.	Exp.	Calcd.	Exp.	Calcd.	Exp.	Calcd.	Exp.
B <sub>2</sub>		1136	1128	1131	1122	1128	1120	1125	1118	1125
E		1105	1104	1100	1103	1099	1103	1098	1103	1095
A <sub>1</sub>		990	986	963	985	962	985	962	984	962
B <sub>2</sub>		767	650	640	633	640	630	636	626	633
E		631	626	610	624	608	623	608	622	610
A <sub>1</sub>		837	549		515		513		500	
B <sub>1</sub>		477	470		464		462		460	
B <sub>2</sub>		595	380		285	262	226	215	201	
E		484	307		240	230	213	195	195	159
A <sub>1</sub>		427	275		198		126		98	
E		160	76		49	62	37		29	

## RESULTS AND DISCUSSION

The procedure adopted in this study concerning the calculation of the thermodynamic functions of a molecule in the vapour phase [5] was described in detail in a previous work [6]. These calculations provide reliable entropy and free energy function values when the vibrational frequencies are determined and structural information defined. Parameters not experimentally available can be obtained from theoretical models.

As concerns the gaseous sulfates, spectroscopic data were available, from recent IR and Raman studies, for  $\text{Na}_2\text{SO}_4$  [2],  $\text{K}_2\text{SO}_4$  [2] and  $\text{Cs}_2\text{SO}_4$  [3,7].

The vibrational spectra were, however, incomplete because a systematic far IR investigation has never been carried out.

We explored the IR spectrum in the range below  $600\text{ cm}^{-1}$  for all the alkali sulfates while IR and Raman spectra of  $\text{Rb}_2\text{SO}_4$  were studied over the whole frequency range from  $1200$  to  $30\text{ cm}^{-1}$ .

The experimental bands observed in the course of this study were assigned on the basis of augmentations, such as metal dependence of the interionic modes resulting in measurable frequency shifts, and doubling of the degenerate vibrations due to the matrix-effect [2,7]. The results of the electrostatic model calculations, performed for all the molecules of this study, confirmed the preliminary assignments. In the high frequency region, regarding the vibrations of the  $\text{SO}_4^{2-}$  group, the assignment was performed in previous works [2,3,7]. A summary of the observed and calculated frequencies is given in Table 1.

Due to the extensive decomposition of the  $\text{Li}_2\text{SO}_4$  molecule, no IR and Raman spectra could be obtained. This fact is indicated in the spectra by the presence of  $\text{SO}_2$  [8] and lithium peroxide bands [9]. The vibrational frequencies and the geometry of this molecule were obtained with the aid of the electrostatic model.

The model describes the potential function in terms of interaction between the  $\text{SO}_4^{2-}$  group and the metal cations  $\text{Me}^+$ . The calculations were performed assuming a  $D_{2d}$  symmetry configuration. The potential function used in the model is in the form

$$U = \sum_{i>j} \frac{Z_i Z_j}{r_{ij}} + \sum_{k \neq p} \beta_{kp} B_0 Z^2 \frac{(r_k + r_p)^{n-1}}{r_{kp}^n} + \sum_{n=1}^{(3N-6)} \frac{1}{2} \lambda_n Q_{n\alpha}^2$$

TABLE 2

Calculated bond distances and angles of gaseous alkali metal sulfates <sup>a</sup>

Molecular parameters	$\text{Li}_2\text{SO}_4$	$\text{Na}_2\text{SO}_4$	$\text{K}_2\text{SO}_4$		$\text{Rb}_2\text{SO}_4$	$\text{Cs}_2\text{SO}_4$	
R(M-O) (Å)	1.88	2.14	2.45	(2.45)	2.55	2.72	(2.80)
R(S-O) (Å)	1.47	1.47	1.47	(1.47)	1.47	1.47	(1.471)
$\angle$ (O-S-O) (°)	108	108	108	(108)	108	108	(108)

<sup>a</sup> Experimental values are given in parentheses (see text for references).

TABLE 3  
 Thermodynamic functions of gaseous alkali metal sulfates ( $\text{J mol}^{-1} \text{K}^{-1}$ )

$T$ (K)	$\text{Li}_2\text{SO}_4$		$\text{Na}_2\text{SO}_4$		$\text{K}_2\text{SO}_4$		$\text{Rb}_2\text{SO}_4$		$\text{Cs}_2\text{SO}_4$	
	$S_T^0$	$-(G_T^0 - H_0^0)/T$	$S_T^0$	$-(G_T^0 - H_0^0)/T$	$S_T^0$	$-(G_T^0 - H_0^0)/T$	$S_T^0$	$-(G_T^0 - H_0^0)/T$	$S_T^0$	$-(G_T^0 - H_0^0)/T$
298.15	308.6	249.1	344.5	274.6	365.4	290.6	393.7	315.3	412.3	331.8
800	428.2	327.6	470.5	362.4	492.8	382.1	521.6	409.3	540.6	427.3
900	445.1	339.7	487.7	375.3	510.1	395.3	538.9	422.7	558.0	440.8
1000	460.5	351.0	503.3	387.4	525.7	407.6	554.6	435.1	573.6	453.3
1100	474.6	361.6	517.6	398.6	540.0	419.0	568.9	446.7	588.0	464.9
1200	487.7	371.6	530.7	409.0	553.2	429.7	582.1	457.4	601.2	475.7
1300	499.8	381.0	542.9	418.9	565.4	439.6	594.3	467.5	613.4	485.9
1400	511.0	389.9	554.2	428.1	576.8	449.0	605.7	476.9	624.7	495.4
1500	521.6	398.3	564.8	436.9	587.4	457.9	616.3	485.9	635.4	504.4

where the first two terms are the electrostatic interaction energy of the  $\text{Me}^+$  ion with the  $\text{SO}_4^{2-}$  rigid group [10]. The third term is the potential energy of the S–O vibrations [11]. The minimization of the potential energy was performed assuming the  $D_{2d}$  symmetry model, that is the stable equilibrium configuration of the gaseous molecules.

The bond distances and angles of the alkali sulfates obtained from the theoretical model are given in Table 2. For potassium and caesium sulfates, the calculated geometrical parameters are compared with the experimental ones [1,4] derived from electron diffraction techniques.

Subsequently, the force constants were obtained as second derivatives of the potential function with respect to the atomic cartesian coordinates [12]. The force constants and the kinetic matrices [13] were employed to calculate the  $(3N - 6)$  vibrational frequencies through the usual methods [13].

The data reported in Tables 1 and 2 were used to calculate the thermodynamic functions listed in Table 3.

As is evident from Table 1, the electrostatic model calculations provide frequencies and geometrical parameters which compare very well with the experimental values. This fact supports the vibrational assignments of the observed frequencies and assures that the uncertainty on the thermodynamic functions due to estimated values can be considered negligible. A further consideration arising from the data reported in Table 2 is that the geometry of the  $\text{SO}_4^{2-}$  group is not affected when it undergoes coordination with different metals.

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