A Re-assignment of the Fundamental Frequencies of Sodium Sulphite

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The vibrational spectrum of sodium sulphite both in the solid state and in aqueous solution has been re-assigned. In the solid state the data are not compatible with point group C_{3v} for the anion and we have rationalised the assignments in terms of the point group S_6. The anomalous results previously reported for the i.r. spectrum of sulphite dissolved in water can be readily interpreted in terms of a chemical reaction between the sulphite anion and the silver chloride windows of the cell.

SEVERAL authors have studied the vibrational spectrum of sodium sulphite [1-4] but the assignment of the observed frequencies to the stretching and bending modes of the sulphite ion is still in a confused state. Using the selection rules for C_{3v} there is an apparent lack of coincidence between the i.r. and Raman frequencies for the fundamental stretching modes of the anion in aqueous solution. Furthermore, there are considerable discrepancies between the i.r. frequencies in the solid phase and in aqueous solution. We have confirmed the i.r. and Raman data in solution and now report a similar lack of coincidence between the i.r. and Raman frequencies in the solid phase. We have rationalised the assignments for the solid state in terms of point group S_6 and the aqueous solution spectra can be re-interpreted if the i.r. spectrum is examined using thin Polythene cell windows.

RESULTS AND DISCUSSION

Vibrational Analysis of Crystalline Na_2SO_3.—The observed i.r. frequencies, which are associated with the fundamental modes of the anion, consist of two strong partially-overlapping bands at *ca.* 1000 and 970 cm^{-1} and two medium absorption bands at 628 and 493 cm^{-1}. These values are in good agreement with the published frequencies.[1,3] In contrast, our solid Raman spectrum shows four sharp lines at 988vs, 950m, 640mw, and 498m cm^{-1}.

The discrepancies are large and unexpected, using the selection rules for point group C_{3v}, but the data can be rationalised in the light of the *X*-ray crystal structure.[5,6] Anhydrous sodium sulphite belongs to space group C_{3i}^1 and there are two molecules per unit cell. The centres of mass of the sulphite ions lie on C_3 sites; two of the sodium ions lie also on C_3 sites but the other two cations are on S_6 sites. The two molecules in the unit cell are related by a centre of symmetry and this provides the key to the lack of co-incidences. The appropriate correlation table and the revised assignment for the fundamentals of the anion are given in Table 1.

TABLE 1

Vibrational analysis of the internal modes of anhydrous sodium sulphite

	Free ion C_{3v}	Site symmetry C_3	Unit cell symmetry S_6	Observed frequencies (cm^{-1}) and assignments	
				Raman	I.r.
ν_1	a_1	a	a_g	988s	
			a_u		*ca.* 1000s,vbr
ν_2	a_1	a	a_g	640m	
			a_u		628m
ν_3	e	e	e_g	950ms	
			e_u		*ca.* 970s,vbr
ν_4	e	e	e_g	498ms	
			e_u		493m

We observed also some weak bands in the i.r. spectrum of the solid at 1133 and 1202 cm^{-1}. Evans and Bernstein [1] assigned these absorptions to the combination and overtone modes, $\nu_2 + \nu_4$ and $2\nu_2$ of the free anion. However, in terms of point group S_6, a large number of overtone and combination modes are allowed and it is not possible to assign the observed bands with any certainty to particular modes.

In addition to the fundamentals of the anion one expects to observe several translatory and rotatory lattice modes at low frequencies in both the i.r. and Raman spectra. We observed a series of very weak

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[2] A. Simon and K. Waldmann, *Z. phys. Chem. (Leipzig)*, 1955, **204**, 235.

[3] C. Rocchiccioli, *Compt. rend.*, 1957, **244**, 2704.

[4] H. Siebert, *Z. anorg. Chem.*, 1954, **275**, 225.

[5] W. H. Zachariasen and H. E. Buckley, *Phys. Rev.*, 1931, **37**, 1295.

[6] L. O. Larsson and P. Kierkegaard, *Acta Chem. Scand.*, 1969, **23**, 2253.

lines between 120—200 cm^{-1} in the Raman spectrum and a broad absorption in the far-i.r. between 100—200 cm^{-1}. The latter is presumably due to a series of overlapping lattice vibrations.

Vibrational Analysis of Na_2SO_3 *in Aqueous Solution.*—Published results [1,2,4] for the solution spectra of sodium sulphite are given in Table 2. The authors have assumed C_{3v} symmetry for the anion and a significant lack of coincidence between the positions of the i.r. and Raman active fundamentals is inferred. We have re-examined the spectra using both water and D_2O as solvents (see Table 2) and our results are in good agreement with those of earlier workers when the i.r. spectrum is examined between silver chloride plates.

TABLE 2

Observed vibrational frequencies for sodium sulphite in aqueous solution (cm^{-1})

Ref. 1		Ref. 2	Ref. 4	Our results	
Raman	I.r.	Raman	Raman	Raman	I.r.
967s,pol.	1002m	966s	968s	966s,pol.	[1010mw] *
933m	954s	925mw	932w	933sh	950s
620w,pol.	632w	612w	618w	620w,pol.	*ca.* 630w
469m	n.o.	471m	465m	473m	n.o.

* Only observed using AgCl windows.

We initially considered several explanations for the lack of coincidence such as: (*a*) the presence of impurities in the sample *e.g.* sulphate, dithionate, *etc.*, (*b*) the occurrence of overtone or combination modes, (*c*) the water molecules are hydrogen bonded to the anion and this results in a lowering of the symmetry from C_{3v}.

However, none of these explanations is necessary if the i.r. spectrum of a strong sulphite solution is examined between very thin Polythene windows. The band at 1010 cm^{-1} is absent altogether and the observed absorptions are then in accord with the Raman spectrum of aqueous solutions. The antisymmetric and symmetric stretching vibrations at 933 and 966 cm^{-1} respectively are two components of the strong i.r. band at 950 cm^{-1} (half-width *ca.* 80 cm^{-1}). Thus we believe that the i.r. and Raman data for sodium sulphite in aqueous solution are consistent and we confirmed the reaction between silver chloride and sodium sulphite by pouring sodium sulphite solution over freshly precipitated silver chloride. The latter was observed to be appreciably soluble and the resulting solution exhibited an i.r. band at 1010 cm^{-1} when examined between Polythene windows. However, the results do not preclude the presence of strongly hydrogen bonded sulphite anions in solution. Sulphite ions are known to be hydrogen-bonded to water molecules in complexes such as $NiSO_3,6H_2O$. The crystal structure of the compound reveals [7] that the site symmetry of the sulphite anion is lowered to C_3 by hydrogen-bonding to the $[Ni(H_2O)_6]^{2+}$ cations. We have examined the i.r. spectrum of the solid complex and the fundamental modes of the anion occur at 972s,vbr; 885s,sh; 655m,vbr; and *ca.* 490vw cm^{-1}. No splitting of the fundamental modes is discernible as anticipated by the site symmetry of the anion.

A similar occurrence of hydrogen-bonding is expected to occur in aqueous solutions and Davis and co-workers [8,9] have observed the effect in the vibrational spectrum of $NaNO_3$ in aqueous solution. The $\nu_3(e)$ fundamental of the nitrate anion is split by 56 cm^{-1} while a splitting of 50 cm^{-1} has been reported for aqueous solutions of Ph_4AsNO_3. The authors were able to demonstrate that when Ph_4AsNO_3 is dissolved in chloroform the solvent is again hydrogen-bonded to the nitrate anion; the ν_3 fundamental consists of a single broad band (70 cm^{-1} half-width) centred on 1360 cm^{-1}. We have attempted to prepare $(Ph_4As)_2SO_3$ in the hope that this salt would enable us to examine the spectrum of the anion in non-aqueous solvents. Unfortunately all our attempts to prepare the salt were unsuccessful.

EXPERIMENTAL

The Raman spectra of anhydrous sodium sulphite (B.D.H.) and saturated aqueous solutions of the salt were obtained using a Cary 81 Raman spectrophotometer fitted with a Coherent Radiation Laboratory model 54 Krypton ion laser. The laser has a power output of 100 mW at a wavelength of 6471 Å.

The i.r. spectra of anhydrous sodium sulphite and D_2O solutions were measured using silver chloride and Polythene (0·04 mm thickness) cell windows on Perkin-Elmer model 125 and 457 spectrometers. The D_2O (99·7%) was supplied by B.D.H. and does not exhibit strong absorption bands over the spectral range 1100—800 cm^{-1}. $NiSO_3,6H_2O$ Was prepared according to the literature method.[7]

[2/520 *Received, 6th March*, 1972]

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