

LETTERS TO THE EDITOR

CRYSTALLOGRAPHIC DATA ON
SODIUM TRIHYDROGEN SELENITE

SODIUM trihydrogen selenite, $\text{NaH}_3(\text{SeO}_3)_2$ is ferroelectric with the Curie point at -79°C .¹ Infra-red and magnetic resonance studies on this compound have been reported,²⁻⁴ but no structural data are so far available. Hence it was thought worthwhile to analyse its structure as part of a programme, undertaken in this department, of systematic X-ray investigation of some ferroelectric crystals.

Transparent platy crystals, elongated along the *b*-axis, of sodium trihydrogen selenite were grown by slow evaporation at room temperature of a saturated aqueous solution of selenium dioxide and sodium carbonate in stoichiometric molar ratio. The unit cell dimensions were determined from oscillation and Weissenberg photographs taken about crystallographic axes using nickel-filtered copper radiation. The following reflections were found to be systematically absent:

$$h0l, h+l=2n+1;$$

$$0k0, k=2n+1.$$

Hence, the crystals were uniquely assigned to the monoclinic space group $P2_1/n$. The density of the sample was measured by flotation in a mixture of methylene iodide and bromoform. The crystal and physical data of the compound are as follows:

Space group—	$P2_1/n$
<i>a</i> =	$10.35 \pm 0.02 \text{ \AA}$
<i>b</i> =	$4.84 \pm 0.02 \text{ \AA}$
<i>c</i> =	$5.84 \pm 0.02 \text{ \AA}$
β =	$89 \pm 1^\circ$
Volume of the unit cell	$= 292.37 \text{ \AA}^3$
Formula weight	$= 279.93$
Number of formula weights	
in the unit cell	$= 2$
Measured density	$= 3.20 \pm 0.01 \text{ gm./c.c.}$
Calculated density	$= 3.18 \text{ gm./c.c.}$
Absorption coefficient for	
X-rays ($\lambda = 1.5418 \text{ \AA}$)	$= 185.5 \text{ cm}^{-1}$.

The multiplicity of general position in the space group is fourfold, and as there are only two $\text{NaH}_3(\text{SeO}_3)_2$ units in the cell, the sodium ion and one of the hydrogens should occupy twofold special sites whereas the HSeO_3 units are at general positions. The complete determination of the structure is under progress.

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Department of Physics,
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Bangalore-12, April 13, 1967.

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NEAR ULTRAVIOLET ABSORPTION
SPECTRUM OF *o*-DIFLUOROBENZENE
IN VAPOUR PHASE

THE absorption spectrum of *ortho*-difluorobenzene molecule in vapour phase has been photographed with the Hilger medium and large quartz spectrographs. Path lengths ranging from 10 to 150 cm. were used. The temperature was varied from 28°C . to 80°C . Hilger hydrogen arc lamp was used as the source of continuous radiation. Ilford N 30 plates were used to record the spectrum. Measurements were made with the help of Hilger Comparator having least count of 0.001 mm, taking iron as standard. The wave numbers are accurate upto $\pm 2 \text{ cm}^{-1}$ for sharp bands and upto $\pm 5 \text{ cm}^{-1}$ for diffuse and broad bands.

This molecule belongs to C_{2v} group symmetry. The region of absorption shows that the electronic transition in question corresponds to the normally forbidden $A_{1g} \rightarrow B_{2u}$ transition of benzene. In the case of the above symmetry the corresponding electronic transition becomes $A_1 \rightarrow A_1$, which is allowed, with the transition moment lying along the X-direction bisecting *ortho* C-C bond. The strong band at 2642.7 \AA (37829 cm^{-1}) has, therefore, been assigned as the 0, 0 band of the system.

Frequency separations 170, 306, 430, 561, 767 and 1032 cm^{-1} (from the 0, 0 band) of bands lying to the longer wavelength side of the 0, 0 band have been taken to be the fundamental vibrational frequencies in the ground state (G.S.). Similarly frequencies 237, 398, 550, 720, 924, 1087, 1265 and 1387 cm^{-1} occurring in

TABLE I

Correlation of Raman, infra-red and ultraviolet ground, excited state frequencies

Raman shifts (liquid)	Depolarisation data	Infra-red frequencies (Vapour)	Band type	Ultraviolet absorption frequencies		Mode of vibration
				G.S.	E.S.	
197 (s)	0.9	170 (s)?
296 (m)	0.89	306 (ms)	237 (s)	Out-of-plane ring bending
436 (w)	0.9	430 (s)	398 (s)	C-F bending i.p.
566 (m)	0.4	567 (m)	A	561 (ms)	550 (vs)	C-C-C bending i.p. (totally sym- metric component $a_{1g}e_{g^+} 606$ in benzene)
762 (vs)	0.2	762 (m)	A	767 (ms)	720 (vs)	C-C ring breathing
1020 (s)	0.1	1024 (m)	A	1032 (vw)	924 (s)	C-C-C trigonal bending
1152 (m)	0.6	1155 (vw)	A	..	1087 (s)	C-H bending i.p.
1269 (s)	0.2	1279 (s)	A	..	1265 (s)	C-F stretching
1469 (vw)	..	1464 (m)	1387 (s)	C-C stretching

Letters in parentheses indicate observed intensities. vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, vw = very weak and i.p. = in plane.

prominent bands on the shorter wavelength side of the 0,0 band have been assigned as the excited state (E.S.) fundamentals.

The ground and excited state frequencies together with corresponding Raman and infra-red¹ frequencies are tabulated in Table I. The agreement can be seen to be quite satisfactory. Some of the prominent frequencies have also been assigned to definite modes.

There are bands at separations of 12, 34, 40, 63 and 96 cm^{-1} on the red side of the 0,0 band. These may be due to ν - ν transitions of the low-lying vibrations in the two states.

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FRANCK-CONDON FACTORS AND r -CENTROIDS OF THE C'-X SYSTEM OF PO MOLECULE

VIBRATIONAL analysis of the bands of the C'-X system of PO lying between 2248 Å and 2958 Å made by Santaram and Rao¹ (1962) revealed the absence of (1,2), (2,0), (2,1), (3,0) and (4,0) bands. The Franck-Condon factors are mainly responsible for the intensity distribution in the vibrational structure of a band system, and it was thought worthwhile to compute these and compare the results with the observations. Recently Sankaranarayan² (1966)

has calculated the r -centroid values and Franck-Condon factors for the bands of the A-X system of PO molecule.

Since for this system $|d\alpha/a| = 0.46\%$, the method of α -averaging outlined by Fraser and Jarman³ (1953) has been employed to evaluate the Franck-Condon factors. Data for the calculation were obtained from Singh⁴ (1959) and Narasimham *et al.*⁵ (1965). The results are given in Table I in parentheses. The r -centroids, $r_{v',v''}$ were calculated by the graphical method developed by Nicholls and Jarman⁶ (1956) and are also shown in Table I along with the wavelengths of R_1 heads taken from the analysis of Santaram and Rao.¹

TABLE I

Franck-Condon factors and r -centroids of the bands of C'-X system of PO

$v' \ v''$	0	1	2	3	4
0	(0.153) 1.529 2290.66	(0.286) 1.560 2356.05	(0.273) 1.593 2425.04	(0.172) 1.626 2497.34	(0.082) 1.658 2573.11
1	(0.267) 1.503 2248.28	(0.120) 1.539 2311.74	(0.000)	(0.294) 1.603 2417.66
2	(0.098)	(0.001)	(0.089) 1.550 2333.84	(0.147) 1.582 2400.83	..
3	(0.071)	(0.065)	(0.055)		
4	(0.054)				

First row: (in parenthesis): Franck-Condon factors.

Second row: r -centroids in A.U.

Third row: Wavelengths of the bands in A.U.

A smooth curve is obtained by plotting $r_{v',v''}$ against $\lambda_{v',v''}$ and it was found that $r_{v',v''}$ increases with λ . The calculated Franck-