

Letters to the Editor.

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The Spectrum of SiF.

IN connection with a forthcoming paper by us on the bond energies of molecules, we found that the existing analysis of SiF bands was by no means complete and satisfactory.¹ We have therefore revised the vibrational analysis of the β -bands and of the α -bands, and added an analysis of the γ -bands. The β -bands can now be ascribed to ${}^2\Sigma \rightarrow {}^2\Pi$, the α -bands to ${}^2\Pi \rightarrow {}^2\Pi$ and the γ -bands to another ${}^2\Sigma \rightarrow {}^2\Pi$ transitions. All these transitions involve the same ${}^2\Pi$ lower level which is also the ground state of the molecule. The constants of the molecule in its various electronic states are:—

Term	ν_0 (cm. ⁻¹)	ω_0	$\omega_0 x_0$	D (Volts)
X ${}^2\Sigma$	0 161.1	852.0	4.7	4.77
A ${}^2\Pi$	23573.9 448.4	674.4	6.9	2.04
B ${}^2\Sigma$	34716.6	1006.4	4.8	6.51
C ${}^2\Sigma$	39531.5	885.5	6.2	3.90

A detailed report of the analysis and the structure of the molecule will be published elsewhere.

R. K. ASUNDI.
R. SAMUEL.
Department of Physics,
Muslim University,
Aligarh,
March 14, 1936.

¹ Cf. Jevons: *Report*.

Hydration and Change in Water Equilibrium in Electrolytic Solutions.

IN continuation of my previous work¹ on the subject, the three strong electrolytes, sodium nitrate, sulphuric and hydrochloric acids, are now studied in their aqueous solutions along with the pure solvent in each case under identical experimental conditions and with times of exposure varying inversely as the quantity of water contained in equal volumes of the solution and the pure solvent with a view to quantitatively estimate the changes that take place in the constitution of water *as solvent* as compared with that of the pure liquid.

It has been found from my earlier investigations that the influence of strong electrolytes on the constitution of water is to shift the water equilibrium between mono-, di- and tri-hydrol as could be inferred from a detailed study of the structure of the Raman water-band in their aqueous solutions. Further, in most of them, the observed effect has been noticed to be complicated by the presence of hydration, which has been found to be least prominent in the case of sodium nitrate. The influence of mono-, di- and tri- or more complex hydrates on the structure of the Raman water-band has been shown elsewhere² to be to intensify approximately the corresponding components of the water-band due to the single, double and triple molecules of water. With a view to supplement the qualitative results hitherto obtained in a number of substances, a quantitative study of some of them is undertaken in the present investigation.

For this purpose, analysis of the intensity curves of the Raman band for water in the pure solvent and in the solution is carried out for each of the electrolytes on the lines of the analysis made by Ramakrishna Rao,³ with the following results:—

Substance	Percentage proportion of		
	(H ₂ O) ₁	(H ₂ O) ₂	(H ₂ O) ₃
I. (a) Water	13.35	56.2	30.45
(b) NaNO ₃ , 8N	27.74	56.4	15.86
II. (a) Water	13.52	56.15	30.33
(b) H ₂ SO ₄ , 7.81N	16.97	50.5	32.53
III. (a) Water	13.7	55.3	31.0
(b) HCl, 7.65N	11.04	69.39	19.56

In the light of the above analysis, the influence of each of the dissolved electrolytes appears to be as follows: while sodium nitrate tends to change trihydrol into monohydrol with no especial effect on the proportion of dihydrol, hydrochloric and sulphuric acids tend to change trihydrol into dihydrol and dihydrol into mono- and trihydrol respectively. Further, in the case of the acids, the observed changes in the distribution of intensity along the water-band also partly arise out of the presence of hydration of the ions of the dissolved substances: thus, while hydrates with two molecules of water of hydration preponderate in the solution of hydrochloric acid, those with one and three or more associated water molecules appear to be present in greater numbers in the solution of sulphuric acid at the same concentration.

A detailed report of the investigation will appear elsewhere.

C. SAMBASIVA RAO.

Andhra University,
Waltair,
February 1, 1936.

¹ *Curr. Sci.*, 1934, **3**, 154; *Ind. Jour. Phys.*, 1934, **9**, 195.

² *Proc. Roy. Soc.*, (A), 1935, **151**, 167.

³ *Proc. Roy. Soc.*, (A), 1934, **145**, 489.

Constitution of Formic Acid and Formates.

In a recent issue of the *Journal of the Indian Chemical Society* Halasyam¹ points out that the calculated parachor value for the Sarkar-Ray formula² for formic acid is in better agreement with the experimental value than

that of the dihydroxymethylene formula of Seshadri.³ He advocates therefore the acceptance of the first formula. He omits, however, to point out that the calculated parachor for the usual formula for formic acid (93.2 units) also agrees with the experimental value (93.3)⁴. The parachor values cannot therefore be employed to support the Sarkar-Ray formula.

T. S. WHEELER.

Royal Institute of Science,
Bombay,
February 27, 1936.

¹ *J. Ind. Chem. Soc.*, 1925, **12**, 813.

² *Proc. Ind. Science Congress*, 1935, 109.

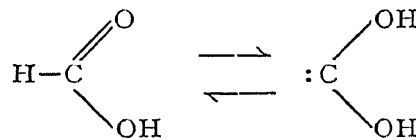
³ *Curr. Sci.*, 1934, **3**, 353.

⁴ See Landolt-Bornstein, 2nd Supplement, 5th Edition, p. 177.

On the Constitution of Formic Acid and Formates.

In the December, 1935, issue of the *Journal of the Indian Chemical Society* (p. 813) received just now, there is a note by Halasyam on the above subject. Referring to my letter to *Current Science*, under the same title 1934, **3**, 353, he writes, "The labile structure is more in the nature of a zealous endeavour to save the classical formulæ of organic chemistry from the ruthless onslaughts of the modern physical chemist with his searching X-ray and spectroscopic analysis. It is probably once again this fervour which actuated the statement, etc." Such remarks are out of place in a scientific controversy.

Halasyam says, "Seshadri disagrees with this view and postulates in its place a labile structure to the acid molecule,



which is apparently meant to do away with the heterodox hypothesis of Ray and Sarkar and yet explain the absence of the well-known Raman line." I would suggest a more careful perusal of my previous letter to *Current Science*. I maintained and still maintain that formic acid has the simple rational constitution

