

## Letters to the Editor.

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## Oxygen in Solar Prominences.

IN *Kodaikanal Observatory Bulletin* No. 107 the existence of oxygen in the solar chromosphere was demonstrated by spectrograms taken in full sunlight. The dismantling of the spectrograph for use at the solar eclipse of June 19th, 1936 makes it opportune to report progress on the results of observations of the oxygen lines in solar prominences. The lines used were the infra-red triplet at  $\lambda$  7770.

When a solar prominence is on the slit of the spectrograph, the oxygen triplet is found to be present, although always very faint. The conditions for photographing the oxygen triplet in a prominence are more easily attained than those for photographing it in the chromosphere since there is less difficulty with the tremor of the sun's limb, but the demonstration of the oxygen triplet reversals in a prominence is less frequently successful on account of the faintness of these lines in prominences compared with the sky spectrum. It is necessary to have a bright prominence and a blue sky to show the oxygen triplet brightly reversed against the sky spectrum.

The best results so far were obtained in a narrow prominence on the 11th December,

1935. The lines of the oxygen triplet were found in this prominence at a height of about 20" above the chromosphere, or 9,000 miles. There was no possibility of these lines being due to chromospheric light, as the reversals were short in length corresponding to the short length of the prominence on the slit.

The photometry of these faint lines in full sunlight will always be a matter of difficulty on account of the presence of the sky spectrum and it seems best to wait until eclipse photographs are available for oxygen lines.

Kodaikanal Observatory, A. L. NARAYAN.  
March 20, 1936. T. ROYDS.

## Absorption Spectra of Halides and Oxyhalides of S, Se, and Te.

IN continuation of earlier work on the chlorides and oxychlorides of sulphur,<sup>1</sup> we have measured the absorption spectra of a number of halides and oxyhalides of S, Se, and Te in the vapour state. The observed maxima of selective absorption together with their long wave limits are listed in Table I and we have added also the bond energies (in K. cal/mol) corresponding to the correlated

TABLE I.

	I Absorption			II Absorption			III Absorption			IV Absorption					
	Red wave lim.		Maximum	Red wave lim.		Maximum	Red wave lim.		Maximum	Red wave lim.		Maximum			
	$\lambda$ ( $m\mu$ )	Kcal/mol	$\lambda$ ( $m\mu$ )	Volts.	$\lambda$ ( $m\mu$ )	Kcal/mol	$\lambda$ ( $m\mu$ )	Volts	$\lambda$ ( $m\mu$ )	Kcal/mol	$\lambda$ ( $m\mu$ )	Volts			
SOBr <sub>2</sub>			378	75	327	3.7	281	101	265	4.6	245	116			
			2 D <sub>B</sub> (S - Br) = 74					2 D <sub>B</sub> (S - Br*) = 95					D (S = O) = 116		
SeCl <sub>4</sub>	(415)	(68)					301	94	275	4.5	(250)	(114)	(240)	(5.1)	
SeOCl <sub>2</sub>							315	90	266	4.6	250	114			
Se <sub>2</sub> Cl <sub>2</sub>			410	69	350	3.5	320	89	295	4.2	249	114	(237)	(5.2)	
			D <sub>B</sub> (Se-Cl) = 47			D (Se <sub>2</sub> ) = 59			2D <sub>B</sub> (Se-Cl) = 94						
SeBr <sub>4</sub>	580	47	490	530	427	2.9	350	81	262	4.7	250	114			
Se <sub>2</sub> Br <sub>2</sub>				465	384	3.2	350	81	322	3.8	288	98	257	4.8	
			D <sub>B</sub> (Se-Br) ~ 42			D <sub>B</sub> (Se-Br*) ~ 53 D (Se <sub>2</sub> ) = 59			2 D <sub>B</sub> (Se-Br) ~ 84			2 D <sub>B</sub> (Se-Br*) ~ 106 D (Se = Se*) = 87			
TeCl <sub>2</sub>	480	59	317				290	98	251	4.9	246	115			
TeCl <sub>4</sub>	480	59	324				272	105	247	5.0					
			D <sub>B</sub> (Te-Cl) = 55			2 D <sub>B</sub> (Te-Cl) = 110									
TeBr <sub>2</sub>	535	53	473	420	380	3.2	340	84	314	3.9	293	97	(238)	5.4	
TeBr <sub>4</sub>	525	54	465		(400?)		296	96	265	4.6	(249)	(114)			
			D <sub>B</sub> (Te-Br) = 48			D <sub>B</sub> (Te-Br*) = 59			2 D <sub>B</sub> (Te-Br) = 96			2 D <sub>B</sub> (Te-Br*) = 124 2 D <sub>B</sub> (Te-Br*) = 108			

processes of photo-dissociation.  $D_b$  denotes values calculated from thermo-chemical data, e.g.,  $D_b$  (Te - Cl) is one quarter of the heat of formation of  $\text{TeCl}_4$  from the gaseous atoms (not from the elements),  $D$  denotes a value taken directly from the band spectra of the diatomic molecules. Wherever a dissociation involves excited products, this is marked by an asterisk against the atom undergoing excitation. Some of the thermo-chemical data, particularly the latent heats of the compounds, are uncertain, and, as discussed elsewhere, it is difficult to determine that value of the long wave limit, which belongs to the molecule in its lowest state of vibration. Considering this, the agreement is very satisfactory.

Similar to the spectrum of  $\text{S Cl}_2$ , the di- and tetrahalides possess different regions of selective absorption in which at first one and then a second halogen atom is split off. From those molecules containing a double bond, e.g., the mono- and oxyhalides, always two halogen atoms are split off simultaneously. The breaking up of the double bond is observed where its energy value comes in the region under observation and the same holds for the dissociation of excited atoms, which can be observed for instance in the second and fourth region of selective absorption of the di- and tetra bromides, the electronic separation of the chlorine atom ( $881 \text{ cm.}^{-1}$ ), being too small to be resolved in the spectrum.

These results confirm entirely the conclusions, drawn from the corresponding photo-dissociations of the chlorides and oxychlorides of sulphur and of other molecules. Furthermore, since the process of photo-dissociation determines the energy value of an individual bond directly, and not as part of a grand total as in thermo-chemical experiment, it can be seen that the bond energies are approximately additive in the same molecule and remain approximately constant in all the di- and tetravalent molecules. This result can hardly be understood otherwise than in a pair bond theory of valency, in which each linkage is produced by a pair of electrons, one from each atom, and localised between them.

A detailed report will be published elsewhere.

S. L. HUSSAIN.

Department of Physics,

Muslim University,

Aligarh,

April 5, 1936.

R. SAMUEL.

<sup>1</sup> R. K. Asundi and R. Samuel, *Proc. Phys. Soc.* (London), **48**, 28, 1936; Mohd. Jan Khan and R. Samuel, *Ibid.*, in Press.

#### Note on the Raman Spectra of Metallic Formates and the Constitution of Formic Acid.

In a recent paper<sup>1</sup> I have shown that the formates of sodium, calcium, cadmium and lead yield Raman lines both in the state of solid and aqueous solutions, the average frequencies of which are 2834, 2732, 1717, 1534, 1347 and  $851 \text{ cm.}^{-1}$ . Besides, in the solids two other frequencies are also present at 2976 and 1397. The frequency shifts in the sodium formate solution have since been confirmed by Edsall.<sup>2</sup> Of these frequencies 2834 was assigned by me to the valence oscillation and 1347 to the deformation oscillation of the HCO group in the formate ion. The origin of the line at 1534 which is of medium intensity in the lead formate crystals was then considered to be uncertain.

In view of the doubt expressed by Halasyam<sup>3</sup> regarding the assignment of 2834 and 1347, I may indicate the following points in support of my conclusion as to the existence of the aldehyde group in the formic acid.

1. In general, the Raman frequencies between 2600–3400 in the organic substances have their origin in the valence oscillations of the X—H bindings.<sup>3</sup> In the case of the formate ion ( $\text{HCO}_2^-$ ), only two forms of X—H are possible, namely, CH (aldehyde group) or OH (Ray-Sarkar<sup>4</sup>). The OH frequency is always higher than 3300 and hence the only possible bond to which 2834 could be ascribed is the CH.

2. The absence of any line at about 3300 even in the fairly intense spectrum of lead formate crystals indicates the non-existence of any OH group in the ion.

3. In the crystals of lead and calcium formates a weak line was present at 2973 which coincides with the CH frequency in the formic acid.

4. In their detailed study of 16 aliphatic aldehydes R.CO.H (with R=H to R=C<sub>9</sub>H<sub>9</sub>) Kohlrausch and Köppl<sup>6</sup> observe " $\omega=1379$  in H.CO.OR and  $\omega=1390$  in H.CO.R sind vermutlich die CH Deformationsfrequenzen des endständigen Wasserstoffatoms; an der Stelle 1390 weisen dementsprechend auch Formamid (H.CO.NH<sup>2</sup>) und Ameisensäure (H.CO.OH) kräftige Linien auf." The corresponding line in all the formates appears