

scientific body in Italy. Great Britain has given him sympathy and encouragement in his work in generous measure and on her hospitable soil Marconi achieved many of his striking successes; the Government of Great Britain created him a G.C.V.O. Equally abundant is the measure of publicity that his work and movements obtain in the popular press of many lands.

The increasing activities and prosperity of his company and its associates are alone sufficient to justify the hope that the years to come will witness further additions to his notable achievements and the wider spread of his fame as one who by his work as scientist and engineer has served humanity truly and well.

R. E.

Molecular Spectra.

A SYMPOSIUM on the subject of "Molecular Spectra" was held in the chemistry hall of the Indian Institute of Science. All contributions to the symposium were received in full in advance, prominent among them being those from Prof. R. Samuel of Aligarh, Prof. Venkatesachar of Bangalore, Prof. K. S. Krishnan of Calcutta, Dr. Ganesan of Nagpur, etc.

In presenting his paper on "The Raman Spectra of Selenates and Selenic Acid", *Dr. Ganesan* discussed the dynamics of the AX_4 model representing the SeO_4 -ion. In the state of solution the lines observed were 342, 415, 835 and 875, while for the crystalline state the same lines occurred sharper but with slightly displaced frequencies. From the data for the solution state and applying Dennison's formulas, the force constants for Se—O and O—O were calculated as 4.72 and 0.59 respectively. The heat of dissociation for Se—O was found to be 86 K. cal. while the corresponding value calculated from thermo-chemical and band spectra data came out as 95 K. cal. The spectrum of selenic acid differed from that of selenates, just as in the case of sulphuric acid and sulphates, there being a greater number of lines which relate now to the molecule H_2SeO_4 .

An interesting discussion followed: *Prof. R. Samuel* pointed out that the heat of dissociation cannot be entirely calculated from the Raman frequency alone, but a factor of anharmonicity in the vibrations must also be considered. The Raman effect at higher temperatures should show the presence of such an anharmonic factor. He also wanted to know whether there was any evidence for the existence of different kinds of Se—O linkages. *Dr. Krishnan* suggested that some of the discrepancies between the two dissociation values might disappear if due corrections were applied for the ionisation energy, etc., in the calculation of the thermal dissociation energy. *Prof. C. V. Raman* opined that the existence of only four lines indicated that the four bonds Se—O were identical, perhaps in particular for such slow infra-red oscillations. He referred to some earlier investigation by *Bhagavantam* on the Raman effect of benzene and carbon disulphide at higher temperatures, where no definite results were obtained. The lines should broaden out and any small shifts in the frequency will be particularly informative. *Prof. Venkatesachar* pointed out that he and *Sibaiya* had observed a shift of the centre of gravity of Raman bands to one side with rise in temperature. *Dr. P. Krishnamurti* remarked how the SeO_4 lines occur as two pairs, while

the SO_4 lines are uniformly spread out. This is due to the heavier Se atom, and the phenomenon is similar in character to that observed with the heavier tetrachlorides as $SiCl_4$ and $TiCl_4$.

Dr. K. R. Ramanathan and *Dr. L. A. Ramdas* then presented a paper on the further extension of the ultra-violet spectrum of the sun. The present limitations due to the ultra-violet absorption band of ozone and of oxygen were analysed in detail, and it was shown that the heights accessible with pilot balloons must be sufficient for the object in view. Accounts of the spectroscopic methods of estimating the amount of ozone present in the atmosphere, and of calculating the height of ozone layer were also given.

A keen discussion followed in which *Prof. Raman* emphasised that generally in fitting a dispersion formula, the possible existence of bands in the extreme ultra-violet should never be neglected. *Dr. Ramdas* referred to the methods of determining the temperature of the ozone layer as being about 500° . *Dr. Ramanathan* in concluding the discussion complained that most reports about absorption spectra did not include sufficient details such as vapour pressure, temperature, etc., required to estimate the amount of substance employed, and consequently the published results could not be used for meteorological purposes.

Prof. R. Samuel presented a lucid account of the present state of knowledge regarding band spectra in general, and explained how a complete analysis of band spectra of diatomic molecules with the help of Franck-Condon diagrams, gives values of the dissociation energy in both the excited and unexcited states, and the harmonic and the anharmonic factors of inter-atomic forces. The anomalous cases where the energy of dissociation increases with the excitation state, and indeed so that the molecule in its ground state might consist of excited atoms, correspond to molecules with free valencies: the usual normal cases correspond to saturated compounds. The dissociation of molecules and their absorption spectra were then discussed and illustrated with the cases of I_2 , CO, CO_2 and the silver halides, and it was particularly shown how $AgCl$ in the vapour state must be a co-valent molecule, and not made up of ions like HCl . The absorption spectra of the alkali halides and of BeO and ZnO and the anomalous cases with free electron valencies such as NO , CaF , CdF , were described in detail, with their Franck-Condon diagrams. It was postulated in this connection that in crystals also, there are co-valent links between

molecules, and that such a postulate will explain the high melting point, etc.

The spectra of many triatomic molecules such as cadmium, zinc and mercury halides show continuous absorption. The atoms here are co-valently bound, while in $PbCl_2$ they can be shown to be electrovalently bound. The spectra of SO_3 , P_2S_5 , PCl_3 , Cl_2O , $SOCl_2$ were then described. They could be divided into two groups, the one such as SO_3 , and PCl_5 in which the optical dissociation energy, D_o is equal to the thermal value D_T , while in the other, such as PCl_3 , D_o is greater than D_T .

The vapours of organic molecules such as CS_2 show the phenomenon of predissociation. In CH_3Cl and other alkyl chlorides, the continuous spectrum is independent of the alkyl chloride, but the band spectrum differs from case to case, and should therefore correspond to the C—x link. The calculated frequency for the link in the excited state is 1090, the corresponding Raman frequency for the unexcited state being 1210. From the spectra of ethylene dibromide, there is evidence for the interaction between the two C—Br linkages. After a brief account of the absorption spectra of organo-metallic compounds the speaker discussed the interesting results obtained with molecules in the state of solution. Here in many cases as with zinc iodide in alcohol the type of binding gradually shifts from co-valent to electro-valent with increasing dilutions presumably due to the influence of the dipole field of the solvent molecules. When other salts are added to the solution the positive or negative ions thus introduced cause characteristic shifts in the band maxima. The influence of the foreign ion can be either of the nature of a Stark effect or of a change in the internuclear distance.

The theory of complex salts was next considered and it was argued that there could be no co-ordinate linkages here, but only the usual type of co-valent links. There can be no octet rule in general, and all the phenomena of valence can be explained on the basis of different grades of the same kind of linkage, *viz.*, co-valent. There can be no single electron link, and the supposed co-ordinate link formed by the lone pair of electrons in the nitrogen atom is not possible, as these electrons are both of 2s type, and with a neutralised spin.

A brief discussion ensued, in which *Dr. Govinda Rau* pointed out that the evidences for the existence of co-ordinate links were quite considerable. The low dipole moment of CO, and the fact that $Ni(CO)_4$ had no moment pointed to the existence of a co-ordinate link between C and O, in addition to the ordinary double bond. With a few more questions by *Prof. Venkatesachar*, *Dr. Krishnan*, and others, the discussion was terminated.

Dr. K. S. Krishnan then presented an account of the extremely interesting results that he has obtained in collaboration with *Mr. Seshan* on the absorption spectra and fluorescence in single crystals of several organic substances containing a number of benzene nuclei and in potassium nitrate containing the flat NO_3 -ion. The absorption in the two planes parallel and perpendicular to the flat molecules showed characteristic differences.

This suggests that the quantum efficiency of photo-dissociation in such crystals may depend upon the polarisation of the light employed. A particularly interesting finding was that traces of impurities such as naphthalene in diphenyl were also oriented in the crystal, and their presence was clearly brought out in the analysis.

Mr. T. S. Subbaraya reviewed the present position of our knowledge of the band spectrum of mercury and gave the results of a new vibrational analysis of five of the band systems which removed the discrepancies between the results of different investigators. A rather unusual fact pointed out by the author was that vibrational levels with vibration quanta which at first increased and then converged to zero were found in the common ground level of these bands which is accepted to be a ($^1S_o + ^1S_o$) state; the other results were, however, shown to be in accordance with theoretical expectations. Since a stable molecule with a strong binding was not to be expected in the case of van der Waals forces alone, the explanation of the levels revealed by the new analysis was to be the subject of further investigation.

In the discussion that followed *Dr. Samuel* remarked that since it is difficult to accept that the ($^1S_o + ^1S_o$) state could possess such vibrational states as those discovered by the author, one might possibly get over the difficulty by assuming the ground state to be a ($^3P + ^1S_o$) state and the others to be also ($^3P + ^3P$) states. *Mr. Subbaraya* replied that even here there would be difficulties since mercury vapour is known to be monatomic.

Mr. Nagendranath gave an account of the refined methods that he has developed for calculating the frequencies of tri-, tetra- and other poly-atomic molecules.

Dr. M. A. Govinda Rau then presented a paper on the comparative study of the Raman spectra of benzene and pyridine and the conclusions that could be drawn regarding the frequencies and modes of vibration of the benzene molecule. The trigonal symmetry of the benzene molecule was emphasised, and it was shown that the Kekule dynamic model for benzene was strongly supported by Raman spectra data. In a discussion that followed *Prof. Raman* and *Mr. Nagendranath* showed the mathematical difficulties in accepting these interpretations which are so widely supported by *Kohlrausch* and several others.

Mr. S. Kulkarni Jatkari gave an account of his experimental work on the Raman spectra of several organic compounds, and the elaborate precautions taken with regard to the purity of the substances employed such as cyclohexane.

Other papers presented to the symposium were taken as read. *Sir C. V. Raman* in winding up the symposium thanked the several contributors and those who took part in the discussions, and referred in particular to *Prof. R. Samuel* whose enthusiastic co-operation in the proceedings made the symposium such a great success. It was also announced that all the papers presented in the symposium would be very soon published in the form of a monograph.

M. A. G.