

THE RAMAN SPECTRA OF SOME METALLIC HALIDES.

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1. Introduction.

THE Raman effect in a large number of metallic halides has been studied in great detail by several investigators with interesting results. Prof. Schaefer¹ was the first to observe that the cubic crystals like Sodium chloride, Potassium chloride, Sodium fluoride, Lithium fluoride and Calcium fluoride do not exhibit any Raman lines. This negative result has been explained by Fermi and Rasetti² in the case of rock-salt, in which they succeeded in obtaining the Raman spectrum of the second order, the first order according to them not appearing because of the equal and opposite changes of polarisability of the neighbouring ions in the crystal lattice. As a result of very careful and systematic investigations in numerous halides of metals in the form of crystals, belonging to different groups in the periodic system, Krishnamurti^{3,4} has arrived at the important conclusion that co-valent bonds are necessary for the production of Raman lines and that the strength of such bonds could be determined from the intensity with which these lines appear. Compounds like Sodium chloride possessing only electro-valent or ionic linkage fail to show any line. These conclusions are amply supported by the results obtained by other experimenters^{5,6,7,8} with aqueous solutions of inorganic halides. Placzek⁹ has pointed out that Krishnamurti's observations are justified on theoretical grounds. This is also in agreement with the fact that while hydrochloric acid, both in the gaseous and liquid states, gives strong Raman lines, a solution of it in ionising solvents gives no lines at all.

¹ Schaefer, Cl., *Zeit. fur. Phys.*, 1929, **54**, 153.

² Fermi & Rasetti, *Zeit. fur. Phys.*, 1931, **71**, 689.

³ Krishnamurti, P., *Nature*, 1930, **125**, 892.

⁴ Krishnamurti, P., *Ind. Jour. Phys.*, 1930, **5**, 113.

⁵ Daure, P., *Compt. Rend.*, 1928, **187**, 940.

⁶ Gerlach, W., *Nature*, 1930, **18**, 182.

⁷ Braune & Engelbrecht, *Z. Phys. Chem.*, 1930, **B10**, 1.

⁸ Braune & Engelbrecht, *Z. Phys. Chem.*, 1931, **B11**, 409.

⁹ Placzek, *Leipziger Vortrage*, 1931, 92.

Thus, besides the information that is obtained regarding the molecular structure of the compounds studied, the Raman spectra observations with salts indicate in a unique manner the nature of the chemical bond between the atoms in them.

The works of the earlier investigators particularly of Krishnamurti^{3,4} and Schaefer¹ in crystals and of Gerlach,⁶ Carelli-Pringsheim-Rosen,¹⁰ Daure¹¹ and Woodward¹² in aqueous solutions have shown that the halides of alkalies and alkaline-earths give no lines and are electro-valent compounds. On the other hand Daure,⁴ Bhagavantam¹³ and others have shown that the halides of many non-metals, metalloids and a few metals, namely carbon, silicon, phosphorus, titanium, tin, arsenic, antimony and bismuth show the Raman spectrum in a marked manner. The metals of the zinc group, namely, beryllium, magnesium, zinc, cadmium and mercury, occupy a position midway between the strongly electro-positive alkalies and alkaline earths on the one hand and the metalloids and non-metals on the other. The Raman spectrum of the halides of these metals should furnish important information regarding their structure and chemical constitution. According to the investigations of Krishnamurti, Braune and Engelbrecht¹⁴ and Woodward¹² the halides of mercury (both mercurous and mercuric) give strong Raman lines while those of zinc and cadmium show either weak or no lines at all. The results so far obtained with the zinc and cadmium halides appeared however to be meagre and a thorough investigation of them appeared desirable. Accordingly, using improved experimental technique, the present writer has obtained the Raman spectra of these substances both in the state of solid and in solution in different solvents. The investigations have been extended also to magnesium chloride, magnesium bromide and aluminium chloride with negative results.

2. Experimental Arrangements.

The investigations were carried out with arrangements similar to the one described by Wood.¹⁵ The experimental tube, 10 inches long and $1\frac{1}{4}$ inch in diameter, containing the solution was held vertically in a stand. The tube was illuminated by three air-cooled low density mercury arcs in pyrex which was specially constructed and sealed off at a very high vacuum. Under

¹⁰ Carelli-Pringsheim-Rosen, *Zeit. fur. Phys.*, 1928, 51, 511.

¹¹ Daure, P., *Compt. Rend.*, 1929, 188, 61.

¹² Woodward, L. A., *Phys. Zeit.*, 1930, 31, 792.

¹³ Bhagavantam, S., *Ind. Jour. Phys.*, 1930, 5, 35.

¹⁴ *Loc. cit.*

¹⁵ Wood, R. W., *Phil. Mag.*, 1928, 6, 729.

these conditions the continuous spectrum from the arc was found to be at a minimum. The scattered light was focussed on the slit of a Fuess glass spectrograph of large dispersion by means of a right-angled prism and a condensing lens. The intensity of illumination was so great and the alignment of the optical parts was so good that the water bands could be seen visually without any difficulty. The same arrangement was found to work well with the solids, the diameter of the tube alone being made smaller for the finer crystalline powders.

The substances were Kahlbaum's or E. de Haen's purest chemicals and were further purified by repeated crystallisation. The aqueous solutions were prepared with water freshly distilled over potassium permanganate and caustic potash. The methyl and ethyl alcohols used in the investigation were carefully purified by distillation over metallic calcium. The solutions were rendered dust-free by two or three filtrations through several layers of filter paper.

3. Results.

The Raman frequencies obtained for these substances are given in Tables I and II. Table III gives the frequencies for the halides of mercury,

TABLE I.
Zinc Halides.

Substance	Exciting line	Raman line	$\Delta\nu$	Intensity
$ZnCl_2$ (70% Aq.)	4358.34	22660	278	Medium, diffuse.
$ZnCl_2$ (50% Aq.)	4358.34	22665	273	„ „
$ZnCl_2$ (30% Aq.)	4358.34	22668	270	Weak, diffuse.
$ZnCl_2$ (30% EtOH)	4358.34	(1) 22644 (2) 22638	294 300	Strong, sharp. Very weak.
$ZnCl_2$ (30% MeOH)	4358.34	22648	290	Medium, sharp.
$ZnCl_2$ (crystals)	4358.34	(1) 22706 (2) 22698	232 240	Medium, sharp. Very weak.
$ZnBr_2$ (100% Aq.)	4358.34 5461.73	22765 18133	173 175	Medium, diffuse. Weak.
$ZnBr_2$ (50% Aq.)	4358.34 5461.76	22770 18138	168 170	Medium diffuse. Very weak.
$ZnBr_2$ (crystals)	4358.34	22778	160	Very weak.

cadmium and zinc for comparison. Exposures varying from 2 hours to 12 hours were given on Ilford Hypersensitive Panchromatic plates, speed 2500 H and D and an iron arc comparison spectrum was photographed on each plate. The wave-length was calculated by linear interpolation from the nearest known lines.

TABLE II.
Cadmium Halides.

Substance	Exciting line	Raman line	$\Delta\nu$	Intensity
CdCl ₂ (50% Aq.)	4358.34	22696	232	Very weak.
CdCl ₂ (crystals)	4358.34 4046.50	22696 24467	242 239	," "
CdBr ₂ (50% Aq.)	4358.34 5461.73	22783 18154	155 153	," "
CdBr ₂ (in excess of KBr)	4046.50	24872 24542	166 164	Medium, diffuse. Strong, diffuse.
	4358.34	23105 22771	167 167	Medium, diffuse. Strong, diffuse.
CdBr ₂ (crystals)	4046.50	24553	153	Weak.
CdI ₂ (25% Aq.)	4358.34 4046.50	22819 24585	119 120	Medium, diffuse. ," "
CdI ₂ (crystals)	4358.34	22826	113	Medium, sharp.
CdI ₂ (in EtOH)	4358.34 4046.50	22806 24575	132 131	Strong, sharp. ," "
CdI ₂ (in MeOH)	4358.34 4046.50	22813 24832 24579	126 126 126	," " Weak. Strong, sharp.
CdI ₂ (in excess of KI)	4358.34	22819	119	Medium, diffuse.
CdI ₂ (in excess of KBr)	4358.34 4046.50	22812 24832 24582	126 126 125	Strong, diffuse. Weak. Strong, diffuse.

4. Discussion of Results.

Among the compounds studied here, Krishnamurti^{3,4} has obtained for crystalline zinc chloride a single *faint* line at 234 cm.⁻¹ with indications of two more faint lines of an extremely doubtful character. The author has obtained for this compound a line of *medium intensity* whose frequency value agrees closely with that given by Krishnamurti and another faint companion

TABLE III.
Raman Frequencies.

Mercuric	Cadmium		Zinc*	
	Author	Others	Author	Others
Solid 313 _s , 381 _w ⁽⁴⁾	240 _w	..	232 _m , 240 _w	234 _w ⁽⁴⁾
Aq. soln. 320 _s ⁽⁷⁾	237 _w	243 _w ⁽¹⁶⁾	278 _m	297 _m , 396 _w ⁽¹⁷⁾
Solid 187 _s ⁽²²⁾	153 _w	..	160 _w	..
Aq. solution	160 _w	..	173 _w	..
Solid	113 _m	105 _w , 345 _w , 395 _w ⁽⁴⁾
Aq. solution	119 _m

S.—s=strong, m=medium, w=weak, vw=very weak.

* index numbers denote references contained in the text of the paper.

the longer wave-length side. In aqueous solutions this line becomes diffuse and is considerably shifted. The line sharpens and gets very less intense as the dilution is increased and a slight shift towards longer wave-lengths is also observed in the less concentrated solutions. In aqueous solutions of zinc chloride of varying concentration, Hibben¹⁷ noted lines at 297 cm.⁻¹ the former shift, according to him, having an intensity approximately six times greater than the latter. In very dilute solutions, the ratio of the intensities became less, the two lines having approximately equal intensity at half molar concentrations. The second of these was found by the present investigator, while the first is somewhat higher than the value 278 cm.⁻¹ found for a 70% solution by the author.

The results obtained for the zinc bromide are similar to those for the iodide, frequency shifts being smaller corresponding to the increased mass of the halogen atoms. A very long exposure of 48 hours for a 15% solution of zinc iodide in water failed to yield any line, but in this case the solution was so intensely coloured that even the green line of mercury was not heavily obscured.

* While this paper was being sent to the press, a note has appeared in the *Journal of Chemical Physics*, 1935, 3, 241, by Salstrom and Harris, giving the Raman frequencies of zinc chloride and zinc bromide in the fused states and the higher frequency shifts given by them are in good agreement with the values obtained by the author for the crystalline substances.

¹⁶ Silveria, *Compt. Rend.*, 1932, 195, 416.

¹⁷ Hibben, *Proc. Nat. Acad. Sci.*, 1932, 18, 532.

Among the cadmium halides, Krishnamurti^{3,4} obtained for cadmium iodide in thin flakes three *weak lines* at 105 cm.^{-1} , 345 cm.^{-1} , 395 cm.^{-1} by the green excitation of mercury which were rendered doubtful by the presence of diffraction lines. But the author has succeeded in getting only one line at 113 cm.^{-1} of *medium intensity* by excitation with the 4046, 4358 and 5461 radiations, and there was no trace of any other line of greater shift. In the solutions of the iodide in different solvents also only one line has been observed. The other halides of cadmium gave one line each, both in solid and solutions; but they were relatively very weak.

From Table III it can be seen that the frequencies obtained for zinc and cadmium are of the same order of magnitude as for the corresponding mercury compounds. There is a progressive diminution of frequencies from chloride to bromide and from bromide to iodide, according to the increased mass of the halogen atom. Crystals of zinc chloride where the line was fairly intense, gave a faint companion as in the case of mercuric chloride. Therefore in all the cases studied the line that has been obtained is presumably due to the symmetrical oscillation of a linear triatomic molecule as has been indicated for the mercuric halides by its Raman spectrum⁴ as well as from the measurements of their dipole moments.¹⁸ From the values of the frequency, the binding force between the metal and the halogen is calculated in each case on the basis of Dennison's theory¹⁹ for the linear triatomic molecule, neglecting of course the repulsive forces between the extreme halogen atoms and is given in Table IV. The frequency shifts in the aqueous solutions

TABLE IV.

Halogen	Zinc	Cadmium	Mercury ²⁰
Chloride	1.6×10^5 Dynes/cm.	1.2×10^5 Dynes/cm.	2.3×10^5 Dynes/cm.
Bromide	1.4×10^5 Dynes/cm.	1.2×10^5 Dynes/cm.	1.9×10^5 Dynes/cm.
Iodide	1.05×10^5 Dynes/cm.	1.5×10^5 Dynes/cm.

have been taken for the purpose of calculation. From Table IV it is clear that the magnitudes of the binding forces are of the same order for zinc, cadmium and mercury and diminish for all the metals in the direction, chloride \rightarrow bromide \rightarrow iodide. The fact that all the halides of zinc and

¹⁸ Stuart, H. A., *Molekul struktur.*, p. 153.

¹⁹ Dennison, *Phil. Mag.*, 1926, 1, 195.

²⁰ Kohlrausch, *Der Smekal-Raman Effect*.

cadmium show Raman lines is indicative of the existence of co-valent linkage in them.

Mention may be made of the fact that the fundamental frequencies of cadmium compounds are lower than those of the corresponding compounds of zinc as is to be expected from the greater atomic weight of cadmium which belongs to the same homologous series as the former; but the frequencies obtained for either of them are considerably lower than those for mercury, in spite of the greater atomic weight of the latter. This is to be attributed, as has been pointed out by Pai,²¹ to the greater stability of the mercury salts and the corresponding greater strength of the co-valent bond between mercury and the halogen atom.

5. Effect of Different Solvents on the Raman Frequencies.

In no case hitherto studied does the Raman frequency vary as much as in the case of zinc chloride and cadmium iodide when dissolved in different solvents. The sharp intense line at 232 cm.⁻¹ in the crystalline zinc chloride was replaced by a diffuse line of medium intensity in water solutions. In methyl alcohol solution the line was less diffuse and had approximately a shift of 290 cm.⁻¹. In ethyl alcohol the line was stronger, sharper and had a shift of 294 cm.⁻¹. Similar observations were made on cadmium iodide for which the crystal gave a sharp line at 113 cm.⁻¹, aqueous solution gave a diffuse line of medium intensity at 119 cm.⁻¹, solution in methyl alcohol gave a line of greater intensity at 125 cm.⁻¹ and solution in ethyl alcohol gave a sharp intense line at 132 cm.⁻¹ with well-defined antistokes. Such shifts have been observed by the previous workers in the case of mercuric chloride also. The presence of similar halogen ions in the solutions seems to have pronounced effects on the intensity of the lines of cadmium halides. Thus the cadmium iodide line which was slightly diffuse and of medium intensity in water solutions, became very intense with well-defined antistokes, in the presence of potassium bromide or potassium iodide, but did not change appreciably in frequency. Similar strengthening of the spectrum was also observed for cadmium bromide in the presence of potassium bromide. Braune and Engelbrecht^{7,22} failed to get any definite line in aqueous solutions of cadmium halides; but obtained intense lines in the solutions of mixtures of cadmium iodide and cadmium bromide and the corresponding alkali halide whose frequency shifts were smaller than those of the alcoholic solutions. They attributed the line in the solutions of the mixtures to the formation of the complex ions of the types CdX_4'' (X=halogen) in them and the

²¹ Pai, N. G., *P. R. S.*, 1935, 149, 29.

²² Braune & Engelbrecht, *Zeit. Phys. Chem.*, 1932, **B19**, 303.

line in the alcoholic solutions to the oscillations of unionised cadmium iodide molecule. But according to the results of these authors and Krishnamurti,²³ with solutions of mixtures of mercury halides and alkali halides, the formation of any complex compound in solution gives a new line whose frequency shift is decidedly smaller than that of the corresponding mercury halide itself. But in the solutions of cadmium halides in the presence of excess of potassium bromide or potassium iodide only the line of almost the same frequency has been obtained as in the solutions of cadmium halide and there was no indication of any feeble line of shorter shift. Secondly, these changes in the position and intensity of the lines in these compounds are similar to those of the zinc chloride which is not known to form any complex compound. From these it is concluded that the Raman effect data of the solutions of cadmium halides do not offer any evidence for the formation of complex ions in them as has been supposed by the previous authors. The increase of the intensity of the lines of cadmium iodide and zinc chloride in the alcohols and of the cadmium halides in the presence of the alkali halides is presumably due only to the lower degree of ionisation of these compounds under those conditions. The change in the frequency shifts as well as in the sharpness of the lines, indicates the great influence of solvent molecules on the possible oscillations of these compounds, the nature of which, however, is not fully understood.

The other halides.—Hibben¹⁷ has reported three frequencies for aqueous solutions of aluminium chloride. In spite of the most careful attempt of the present writer no line was observed in the crystalline solid or in the solutions of this compound either in water or in ethyl alcohol. But there was a great strengthening of the middle band of water followed by a weakening of the two other bands. Aqueous solutions of the chloride and bromide of magnesium also showed no line and an effect similar to that of aluminium chloride was produced by them in the water band.

In conclusion, the author wishes to express his best thanks to Prof. Sir C. V. Raman, for his kind and helpful guidance in the course of the present work. His thanks are also due to Dr. P. Krishnamurti for his keen interest in the work.

6. Summary.

The paper describes the results of the study of the Raman spectra of the halides of cadmium and zinc as well as of magnesium chloride, magnesium bromide and aluminium chloride. All the halides of cadmium and the chloride and bromide of zinc have yielded lines which show the

²³ Krishnamurti, P., *Ind. Jour. of Phys.*, 1931, 6, 7.

existence of homopolar binding in them. The spectra of zinc chloride and cadmium iodide were fairly intense in contrast to the weak and doubtful lines obtained by the previous investigators, and indicate a linear triatomic model for them analogous to those of mercuric halides.

Marked differences in intensity, sharpness and frequency have been observed in zinc chloride, cadmium bromide and cadmium iodide from crystal to solution and with different solvents. The presence of halogen ions in solution also affect the characteristics of the spectra considerably. These are explained partly by the change in the degree of ionisation in different solvents and partly by the influence of the solvent molecule on the fundamental oscillation frequencies of these compounds. It has been pointed out that the Raman effect data obtained for the cadmium halides do not furnish sufficient evidence for the formation of complex ions of the type CdX_4^- in solution.

Magnesium chloride, magnesium bromide and aluminium chloride gave no Raman lines. A pronounced effect on the bands of water was noticed in each case.

