

THE RAMAN SPECTRA OF SOME INORGANIC COMPOUNDS.

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1. Introduction.

THE Raman frequencies of simple molecules have been of great help in the past in verifying the dynamical theory of molecular vibrations and Placzek's polarisability theory of the Raman lines. The complete spectra of these substances often give valuable clue to the ultimate structure of their molecules. In the course of the investigations of the author on the Raman spectra in the field of inorganic chemistry, which has appeared in these *Proceedings* during the past four years, he has obtained some new unpublished results in the spectra of telluric acid, and of the chromate, molybdate, tungstate, periodate, bisulphate, chlorate, bromate and azide ions as both solids and aqueous solutions. The present paper gives a discussion of these results in relation to the structural properties of these compounds.

2. Experimental.

The substances included in the study were Kahlbaum's extra-pure chemicals and were purified and obtained in good crystalline form by slow crystallisation from the solution of these salts in distilled water. A Fuess spectrograph with a dispersion of about 20 Å and a Hilger two-prism spectrograph with a dispersion of 28 Å in λ 4358 region were used in the investigation. The exciting lines are λ 4046 and λ 4358 of the mercury arc except for the chromates for which the green line λ 5461 was used. For sodium azide and telluric acid crystals, Ananthakrishnan's (1937) technique of complementary filters was employed. The plates were measured by means of a Hilger cross-slide microscope in comparison with an iron arc spectrum.

3. Results.

The results of the investigation are given in Tables I-VI along with the visual estimates of intensities of the lines. The letters in the tables have the following significance: *sh* = sharp, *d* = diffuse, *b* = broad, *vb* = very broad, *st* = strong, *m* = medium intensity, *w* = weak, P = polarised ($\rho < 6/7$) and D = depolarised ($\rho = 6/7$). The concentration of the aqueous solutions is expressed in grams of salt per hundred grams of water.

TABLE I. Telluric Acid (Raman Frequencies in cm.^{-1}).

State of substance	ν_1	ν_2	ν_3	O—H	$k^i \times 10^{-5}$ dynes/cm.	$k^{ii} \times 10^{-5}$ dynes/cm.	$\frac{k^i + k^{iii}}{l^2} \times 10^{-5}$ dynes/cm.
$\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ crystals	670 (10 <i>sh</i>)	657 (0)	365 (2)	3121 (0 <i>b</i>)	3.97	0.054	0.283
H_2TeO_4 26% aq. solution	647 (10) P	624 (1 <i>b</i>) D	357 (3 <i>b</i>) D	Water band	3.54	0.091	0.251

TABLE II. AX_4 Ions (Raman Frequencies in cm.^{-1}).

No.	Substance	ν_1	ν_2	ν_3	ν_4
1	Na_2CrO_4 (crys.) ..	859 (7)	491 (1)	863 (1)	504 (0)
2	Na_2CrO_4 46% solution	859 (10)	481 (2)	874 (0 <i>d</i>)	503 (1)
3	K_2CrO_4 (crys.) ..	859 (6)	486 (1)	877 (0)	513 (0)
4	K_2CrO_4 60% solution ..	853 (10)	486 (3 <i>d</i>)	879 (1 <i>b</i>)	513 (1)
5	$(\text{NH}_4)_2\text{CrO}_4$ 20% solution ..	838 (5)	483 (0)	?	?
6	$(\text{NH}_4)_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (crys.)	936 (10)	218 (2)	915 (1) 893 (3) 874 (0)	360 (1)
7	$(\text{NH}_4)_2\text{MoO}_4$ saturated solution	944 (10)	218 (3)	896 (4 <i>b</i>)	367 (2 <i>b</i>)
8	Na_2MoO_4 saturated solution	897 (3)	241 (0)	841 (1 <i>b</i>)	317 (4 <i>b</i>)
9	Na_2WO_4 40% solution ..	934 (10)	325 (4 <i>b</i>) 50 cm.^{-1} broad	840 (2)	452 (0)
10	KIO_4 crystals ..	795 (10)	277 ($\frac{1}{2}$) 295 ($\frac{1}{3}$)	828 (0) 842 (3) 851 (1)	337 (2) 349 (1) 736 (0 <i>d</i>) ?
11	KHSO_4 anhydrous solid	944 (4) 1026 (6)	455 (3 <i>b</i>)	1187 (1) 1240 ($\frac{1}{2}$) 1360 (0)	737 (0 <i>d</i>) 853 (1)
12	H_2SO_4 (50%) ..	982 (2) 1038 (5)	426 (3)	1172 1234 1341	588 (4) 897 (3)

TABLE III. (*Force constants of AX₄ ions*).

No.	Ion	ν_1	ν_2	ν_3	ν_4	$f \times 10^{-5}$ dynes/cm.	$f' \times 10^{-5}$ dynes/cm.	$P \times 10^{-5}$ dynes/cm.
1	CrO ₄ "	859	481	877	503	4.82	0.53	1.64
2	M ₀ O ₄ "	936	218	896	360	6.1	0.61	0.09
3	WO ₄ "	934	325	840	452	4.5	0.92	0.07
4	IO ₄ '	795	286	842	343	4.6	1.14	0.74
5	SO ₄ "	835	342	875	415	4.22	0.59	0.51

TABLE IV. *AX₃ Ions (Raman Frequencies in cm.⁻¹)*.

No.	Substance	$\nu_1 \parallel$	$\nu_2 \parallel$	$\nu_3 \perp$	$\nu_4 \perp$
1	BaClO ₃ (crys.) ..	910 (0) 930 (10)	492 (0)	..	612 (0)
2	KClO ₃ (crys.) ..	915 (1) 929 (10)	478 (3) 493 (0)	977 (4)	615 (1)
3	KClO ₃ 7% solution	930 (10)	478 (4)	977 (1)	?
4	NaClO ₃ (crys.)	905 (2) 930 (5)	495 (1)		615 (0)
5	NaClO ₃ 100% solution	927 (10)	473 (5 b)	971 (2 vb)	611 (3b)
6	Mg (BrO ₃) ₂ crystals	789 (0) 799 (10)	334 (0) 368 (1 b)	828 (0)	
7	KBrO ₃ crystals	778 (3) 796 (10)	333 (1) 357 (2)	813 (1) 830 (2)	452 (0)
8	KBrO ₃ 6% solution	796 (5)			
9	NaBrO ₃ crystals	797 (10)	357 (2) 378 (2)	822 (0) 842 (3)	452 (1)
10	NaBrO ₃ 45% solution	806 (10)	346 (3)		461 (0)
11	LiIO ₃ crystals	765 (10) 781 (3)	332 (1) 309 (6)	813 (1) 799 (6)	459 (0)

TABLE V. (Force constants of AX_3 ions.)

No.	Ion		ν_1	ν_2	ν_3	ν_4	$f \times 10^{-5}$ dynes/cm.	$f' \times 10^{-5}$ dynes/cm.	β
1	ClO_3'	Author	930	615	977	478	7.26	3.79	$53^\circ-18'$
		Shen and others	930	610	982	479	5.55	6.42	54°
2	BrO_3'	Author	799	452	842	357	6.73	1.07	$55^\circ-30'$
		Shen and others	806	421	836	356	5.25	3.52	$53^\circ-30'$
3	IO_3'	Author	744	423	796	320	6.15	0.27	55°
		Shen and others	779	390	826	330	5.35	3.19	$53^\circ-18'$

TABLE VI. Azide Ion (Raman Frequencies in cm^{-1}).

No.	Name of author	State of substance	ν_2	ν_1	ν_3	$2\nu_2$
1	Author	NaN_3 (solid)	636 (0)	1356 (10)	2077 (0)	1267 (2)
2	Author	NaN_3 saturated solution	?	1346 (10) P	2066 ($\frac{1}{2}$)	1260 (2)
3	Langseth & others	NaN_3 saturated solution		1348 (st)		1258 (vw)
4	Kohlrausch & Engler	HN_3 liquid		1300 (1)	2389 ($\frac{1}{2}$)	

4. Discussion of Results.

1. *Telluric acid*. $H_2TeO_4 \cdot 2H_2O$.—Nisi (1929) has reported one Raman line of medium intensity at 848^1 for a 15 per cent. aqueous solution of telluric acid, and has attributed it to the 'breathing oscillation' of the tetrahedral ion TeO_4'' . In the present investigation both the solid and aqueous

¹ The numbers in these pages signify wave-numbers in cm^{-1}

solutions of this acid has yielded four lines,² (Table I), out of which the broad band at 3121 obviously belongs to the O-H group. The frequency of this linkage is too low to be attributed to the free water of crystallisation and as has been pointed out in an earlier paper (Venkateswaran, 1938), it is characteristic of the O-H group involved in a hydrogen bond. The absence of the well-known bands of the water of crystallisation (Ananthakrishnan, 1937), in telluric acid indicates that the two molecules of water in the crystals of $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ do not remain as such in the compound, but goes to form the molecule $\text{Te}(\text{OH})_6$. If this molecule has octahedral symmetry, it would have three normal modes of vibration, which are active in the Raman effect. Out of these three, one corresponds to the symmetrical oscillations of the molecule and is single and would appear as a very intense and polarised Raman line. Of the other two, one is doubly degenerate and the other is triply degenerate and they would appear as weak, diffuse and depolarised Raman lines. The spectrum obtained for telluric acid, both in the solid and in aqueous solution, clearly indicates that it is octahedral in structure. The study of polarisation of these lines has shown that the intense line at 647 in the solution is more or less completely polarised and therefore, belongs to the symmetrical oscillation ν_1 . The other two frequencies 624 and 357 are depolarised and have to be assigned to the doubly degenerate frequency, ν_2 , and to the triply degenerate frequency ν_3 , respectively. These three lines of the solution are shifted to higher frequencies in the solid state.

Nagendra Nath (1934) has worked out the theory of the oscillations of octahedral molecules and given the following relations for the frequencies ν_1 , ν_2 and ν_3 .

$$\nu_1 = \frac{1}{2\pi c} \sqrt{\frac{1}{m_B} (k + 4k^{ii} + 2k^v + 4k^{vi})} \quad (\text{I})$$

$$\nu_2 = \frac{1}{2\pi c} \sqrt{\frac{1}{m_B} (k + k^{ii} + 2k^v - 2k^{vi})} \quad (\text{II})$$

$$\nu_3 = \frac{1}{2\pi c} \sqrt{\frac{1}{m_B} \left(4 \frac{k^i + k^{iii}}{l^2} + 2k^{ii} \right)} \quad (\text{III})$$

where m_B is the mass of the peripheral atoms. Neglecting the constants k^v and k^{vi} which are usually small, the primary valence constant k , the repulsion constant k^{ii} , and the sum of the directed valence constant and the

² A reference to the spectrum of telluric acid and its structure was made by the author in *Curr. Sci.*, 1937, 6, 5. Subsequently, Gupta (*Nature*, 1937, 140, 685) has also reported three lines for the aqueous solution.

intravalence constant, $\frac{k^i + k^{iii}}{l^2}$, may be calculated from a knowledge of the three Raman-active frequencies. These constants for Te (OH)₆ are given in Table I and are of the right order of magnitude. Though the frequencies in the solid and the aqueous solutions vary slightly, these three constants are approximately the same in both cases, thus indicating that the molecule preserves its identity throughout. It may be mentioned that the spectrum of telluric acid is strikingly different from those of its homologues, *viz.*, sulphuric acid and selenic acid (Venkateswaran, 1936).

AX₄ Ions.

Molecules of the AX₄ type have nine normal modes of vibration and have been treated theoretically by Nagendra Nath (1934) in an exhaustive manner. If they possess tetrahedral symmetry, they reduce to four; the oscillation corresponding to the totally symmetric mode ν_1 is single and polarised, ν_2 is doubly degenerate and ν_3 and ν_4 are triply degenerate. All the four modes of vibrations are active in the Raman and only ν_3 and ν_4 are active in the infra-red spectra.

1. *Chromate ion.*—The Raman spectrum of 13 per cent. aqueous solution of sodium chromate has been studied by Nisi (1929) and has yielded one diffuse line of medium intensity at 855. In the present investigation, the spectra of the sodium, potassium and ammonium salts have been obtained both in the solids and in the aqueous solutions. In general, four frequencies have been observed, of which the line at 859 is sharp and very intense. It is accompanied by a comparatively faint line at about 877. Nisi has probably observed these two together as a single *diffuse* line. Of the other two lines, 486 is more intense than 503. The spectra indicate that the chromate ion is tetrahedral and the probable assignment of the lines are given in Table II. The force constants of the ion are calculated on the basis of Dennison's (1926) formulæ and entered in Table III. The infra-red frequency, 870, observed by Taylor (1929) in K₂CrO₄ is to be attributed to ν_3 and agrees well with the corresponding Raman frequency 877.

Molybdates and Tungstates.—The Raman spectra of molybdates and tungstates have received fair attention in the past. The reported frequencies are grouped together in Table VII along with those of the author. The results of the author agrees well with those of the others, except that in the crystals of ammonium molybdate, the triply degenerate frequency ν_3 at 881 is observed as three lines 915, 893 and 874 on the author's plate. The frequencies reported by Ghosh and Das (1932) for sodium tungstate solution do not appear to be correct.

The Raman spectra of molybdates and tungstates have been the subject of a recent note in *Nature* by Gupta (1937) and his results are given in Table VII. Besides the compounds cited above he has reported more or less similar frequencies for K_2MoO_4 and K_2WO_4 solutions. He has, however, been able to record only three frequencies for the aqueous solutions of molybdates and tungstates and therefrom he has concluded that these ions which

TABLE VII.

Substance	Author	ν_1	ν_2	ν_3	ν_4
$(NH_4)_2MoO_4$ crystals	P. K.	932	216	880	356
	G. J.	927	223	881	362
	C. S. V.	936	218	915 893 874	360
$(NH_4)_2MoO_4$ solutions	N.	943	..	890	..
	G. and D.	938	256	885	356
	G. J.	895	..	820	326
	C. S. V.	944	218	896	367
Na_2MoO_4 solution	N.	898	..	845	330
	G. J.	891	..	823	319
	C. S. V.	897	241	841	317
Na_2WO_4 solution	G. and D.	931	371	1017	(583)
	G. J.	929	320	834	..
	C. S. V.	934	325	840	452
$CaWO_4$ (Scheelite)	N.	909	332	852 835 795	400

P. K.—Krishnamurti, P., 1930; G. J.—Gupta, J., 1937; C. S. V.—Venkateswaran, C. S., this paper; N.—Nisi, H., 1929; G. and D.—Ghosh and Das, 1932.

are di-hydrates in solution are hexa-co-ordinated octahedral units. In support of his conclusion, he has deduced an expression $\nu_1^2 = \nu_2^2 + \frac{8}{3} \nu_3^2$ for octahedral symmetry and indicates that this relation is 'strikingly obeyed, the deviation (2 per cent. for molybdate and 0.1 per cent. for tungstate) being very much less than what has been observed in some accepted octahedral molecules like the hexafluorides of S, Se and Te (10-17 per cent.)'. From Nagendra Nath's formulæ for octahedral molecules given in the earlier part of this paper, we get, neglecting k^v and k^{vi} ,

$$4 \pi^2 c^2 m_{\beta} \nu_1^2 = k + 4 k^{ii} \quad (\text{IV})$$

$$4 \pi^2 c^2 m_{\beta} (\nu_2^2 + \frac{8}{3} \nu_3^2) = k + 4 k^{ii} + \frac{6 (k^i + k^{iii})}{l^2} \quad (\text{V})$$

$\frac{k^i + k^{iii}}{l^2}$ has a value which is nearly equal to (in some cases greater than) k^{ii} and therefore, it is not justifiable to conclude that the equations (IV) and (V) are equal. Hence the relation connecting ν_1 , ν_2 and ν_3 used by Gupta to examine octahedral symmetry in molybdates and tungstates is not valid and the reported agreement goes rather to disprove the possibility of any such structure for these ions. Secondly, assuming that the water of crystallisation is co-ordinated to the metallic ion, this co-ordination will exist in the hydrated crystals as well. In the case of the dihydrate of ammonium molybdate crystals, Gupta has confirmed the results of Krishnamurti (1930) and reported four lines which indicate a tetrahedral symmetry for the ion. Thirdly, in the present investigation, strong solutions of ammonium and sodium molybdates have yielded four lines as in the crystal state and shows that Gupta's results are incomplete. The spectrum of sodium tungstate resembles the spectrum of molybdate; but the frequency ν_4 .452 being generally very weak, is partly obscured by the continuous spectrum accompanying the picture which could not be avoided even after carefully purifying the substance by repeated crystallisations and hence could not be measured accurately. In scheelite (CaWO_4) Nisi (1935) has obtained this frequency and his results are given in Table VII. These results are strongly in favour of a tetrahedral structure for these two ions. The force constants calculated on this basis are given in Table III, and it may be seen that they are of the proper magnitude.

Potassium periodate.—A weak aqueous solution of potassium periodate has been studied by Nisi (1929) and he has reported one Raman line of medium intensity at 702. In KIO_4 crystals Krishnamurti (1930) has observed two lines, 794 (*st*) and 841 (*f*). In the present investigation, the crystalline KIO_4 has yielded nine lines and their frequency shifts are given in Table II. On the assumption that IO_4' ion is very nearly a tetrahedron, the frequencies

are classified in four groups. From the table it is clear that the 'breathing frequency' is given by $\nu_1 = 795$ (10), the doubly degenerate frequency ν_2 is split up into two, 277 and 295, one of the triply degenerate frequencies, ν_3 , is split up into three lines, 828, 842 and 857 and the other one ν_4 has yielded three lines, 337, 349 and 736. The exact origin of 736 is, however, doubtful. These results indicate that the ion is approximately tetrahedral, but slightly distorted in the crystal lattice, resulting in the removal of the degeneracies. The average of these frequencies for ν_1 , ν_2 , ν_3 and ν_4 is made use of to calculate the force constants for the ion given in Table III. The frequency reported by Nisi (1929) for the solution does not agree with any of the lines in the crystal.

Potassium bisulphate.—This substance has been studied by Nisi (1929) as a 28 per cent. aqueous solution and he has obtained the following Raman frequencies: 427 (*f*), 593 (*f*), 978 (*m*) and 1048 (*st*). The spectrum of the anhydrous solid has yielded eight lines and differs from that of the solution, but closely resembles that of 50 per cent. sulphuric acid (Woodward and Horner, 1934) as may be seen in Table II. This clearly shows that 50 per cent. sulphuric acid is predominantly HSO_4' ions.

AX_3 Ions.

The fundamental vibrations of the molecules of the AX_3 type have been treated by Dennison (1926); for pyramidal molecules, there are four normal modes of vibration, two of the normal frequencies ν_1 and ν_2 , being single and parallel to the symmetry axis and the other two ν_3 and ν_4 being perpendicular to the axis and doubly degenerate. All the four vibrations are active in the Raman effect and in infra-red absorption. In a previous communication (Venkateswaran, 1935), the author has shown that the Raman spectra of alkaline iodates indicate that they are pyramidal in structure.

Chlorates and Bromates.—The Raman frequencies of these ions have been determined by Krishnamurti (1930) from the spectra of the crystals of sodium and potassium salts. Sodium and cadmium bromates have been examined by Schaefer, Matossi and Aderhold (1930) and aqueous solutions of sodium chlorate by Dickinson and Dillon (1929). Table IV gives the results obtained by the author for these ions both as crystals and solutions and contains a number of new lines not reported before.

Recently, Shen, Yao and Ta-You Wu (1937) have studied the polarisation of the Raman lines in 10 N \cdot NaClO_3 , 3N \cdot NaBrO_3 and 6.1 N \cdot HIO_3 solutions. Though they were not able to record the four characteristic Raman lines well separated from each other in these compounds, they have deduced the four frequencies from the variation in the degree of depolarisation of

different parts of the individual lines. Parodi (1937) has supported the conclusions of the above authors by his observations in the infra-red absorption of chlorate, bromate and iodate ions. In the present investigation, these four frequencies have been recorded for a few chlorates and bromates in the state of solid and of aqueous solutions. In the solution of the bromate, however, the frequency ν_3 is not resolved from the intense line due to ν_1 . But in the crystalline state the lines are sharp and hence all the frequencies could be identified. The force constants and the angle of the pyramid are calculated according to Dennison's formulæ and given in Table V. The classification of the frequencies by the Chinese workers is also given for comparison. The angle of the pyramid has a fairly constant value of 55° for all the three halogenates. The valence force, f , is the greatest in ClO_3' and the least in IO_3' as could be expected from the relative stabilities of these ions. In the case of iodic acid, the latter authors have attributed the line 826 to ν_3 ; but as has been shown by the author (Venkateswaran, 1934) this line is present only in iodic acid and not in alkaline iodates and is more appropriately assigned to the polymerised group $\text{I}_2\text{O}_6''$. The latter conclusion is confirmed by the fact that this line is observed to be polarised (Venkateswaran 1936), while ν_3 should be completely depolarised:

The main parallel vibration, ν_1 , is split up into four sharp lines in the crystals of Na, K and Li iodates (Venkateswaran, 1934), and has been tentatively explained as due partly to positional degeneracy of the pyramid and partly to accidental degeneracy $\nu_1 = \nu_2 + \nu_4$. It is more probable that the first two lines in this group, represent ν_1 and the last two ν_3 . On the basis of this the average frequencies for the IO_3 pyramid are $\nu_1 = 744$, $\nu_2 = 423$, $\nu_3 = 796$ and $\nu_4 = 320$. From Table IV, it may be seen that ν_1 , ν_2 and ν_3 in all the three halogenates are split up into two lines in the crystals. The splitting of the doubly degenerate frequency, ν_3 , may be explained as due to a slight distortion of the ionic group in the lattice. But the splitting of the single and parallel vibrations, ν_1 and ν_2 , cannot be due to this cause and is probably due to the positional degeneracy pointed out in connection with the iodates. The splitting of single, symmetrical Raman lines in crystals is significant and deserves further investigation.

The Azide Ion.

The structure of the azide ion has been the subject of considerable discussion in recent years. Penny and Sutherland (1936) have summarised the existing evidence furnished by the infra-red and the Raman spectra and by the X-ray studies of azides. The two most probable structures for this

ion about which the decision should lie are (1) the linear and symmetrical form, $\bar{N} = \overset{\dagger}{N} = \bar{N}$, and (2) the linear and unsymmetrical form, $N \equiv N = \overset{\dagger}{N}$. The X-ray studies of cyamuric triazide (Knaggs, 1935) is in support of the second formula. In both these forms, there are three normal modes of vibration; ν_1 and ν_3 are valence oscillations and ν_2 is a deformation oscillation. For the linear and symmetrical model, ν_1 is active in the Raman effect, but inactive in infra-red, while ν_2 and ν_3 are forbidden in Raman and allowed in infra-red spectra. If it were linear and unsymmetrical, all the three frequencies would be active both in the Raman and in the infra-red spectra. Garner and Gomm (1931) have obtained two ground frequencies, 1352 and 2040, for β lead azide in the infra-red absorption. The Raman spectrum of sodium azide solution has been studied by Langseth, Nielsen and Sørensen (1934) and they have obtained two lines 1348 and 1258 (1348 being a hundred times stronger than 1258). They have attributed 1348 to the valence oscillation ν_1 and 1258 to the overtone of ν_2 . From the non-appearance of ν_2 and ν_3 in their spectra, they have concluded in favour of the linear symmetrical form. This conclusion, however, cannot explain the appearance of ν_1 in β lead azide in its infra-red absorption. In a recent paper Engler and Kohlrausch (1936) have recorded two lines, 1300 (1) and 2389 ($\frac{1}{2}$) for hydrazoic acid (HN_3) and concluded that the N_3 group is linear, but unsymmetrical. In the present investigation, four lines are obtained for NaN_3 in the solid state and three lines in the aqueous solution. The strongest line in the two spectra has almost the same frequency as reported by Langseth and others. The line 636 in the solid and 2066 in the solid and solution are extremely weak, but are positively present in the clear and intense plates. In comparison with the infra-red, we have to attribute 636 to the deformation vibration ν_2 and 2066 to the valence oscillation ν_3 . These results are in support of the linear and unsymmetrical form (2). On this model the force constants f_{12} , f_{23} , and f_{13} as calculated come out to be 8.8×10^5 , 15.7×10^5 and 1.3×10^5 dynes/cm. respectively. The magnitude of these constants strongly support the view given above. The ν_1 frequency in the solid is distinctly higher than that in the solution and shows the influence of the crystal forces on the vibrations of the ion.

In conclusion the author wishes to express his humble thanks to Prof. Sir C. V. Raman for his kind interest in the work.

Summary.

The Raman spectra of telluric acid, and the chromate, molybdate, tungstate, periodate, bisulphate, chlorate, bromate, and azide ions are obtained. From these spectra, $\text{Te}(\text{OH})_6$ is shown to be octahedral, CrO_4^{2-} , MoO_4^{2-} , WO_4^{2-}

and IO_4' ions as tetrahedral, ClO_3' and BrO_3' ions as pyramidal and N_3^- as linear and unsymmetrical, in structure. The splitting of the frequencies due to the removal of degeneracy by distortion of ions in the crystals, are observed in a few cases.

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