

RAMAN EFFECT IN SELENIC ACID AND SOME SELENATES.

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1. Introduction.

THE Raman spectra of symmetrical tetrahedral molecules of the type AX_4 have been extensively studied both experimentally and theoretically in relation to their fundamental frequencies of oscillation. The various tetrahalides like CCl_4 , CBr_4 , etc., among the organic compounds, and aqueous solutions of salts containing RO_4 ions among the inorganic ones, are the important compounds of this class that have been studied. Among the latter the study of the sulphates has received special attention from many investigators, whereas the available data for the allied compounds, the selenates, are very meagre indeed. Only two measurements are available, one by Nisi¹ who studied a 17% solution of sodium selenate and records three frequencies, and the other by Schaeffer, Matossi and Aderhold² who obtain with magnesium ammonium selenate only the prominent frequency of the SeO_4 ion, of about 830 cm.^{-1} The infra-red spectrum of the selenates has been studied by Schaeffer and Schubert³ who get a reflection maximum at $11.20\ \mu$ which is analogous to the maximum at $8.82\ \mu$ obtained in the case of the sulphates. The present paper describes the study of the Raman spectra of a number of selenates both in the crystal state and in the state of solution, and also of selenic acid.

2. Experimental.

The substances were all recrystallised, and for the preparation of the solutions pure water distilled under low pressure was used. These precautions were found necessary as otherwise there was an appreciable continuous spectrum in scattering probably due to fluorescent impurities, which masked the feeble Raman lines. In the case of the sodium and potassium selenates the solutions studied were of about 30% strength, and with ammonium and magnesium selenates of about 20%. Thallous selenate is only sparingly

¹ *Jap. Jour. Phys.*, 1929, **5**, 119.

² *Zeits. f. Phys.*, 1930, **65**, 314.

³ *Zeits. f. Phys.*, 1921, **7**, 297.

soluble in water (to the extent of about 2%) and hence the Raman lines were not brought out in solution.

The experimental technique for the study of the Raman spectra of crystals and solutions is too well known to need description here. In the present measurements, a Fuess glass spectrograph of large dispersion was used. The Raman frequencies obtained are collected together in Table I.

TABLE I.

Intensity	Aqueous Solution				Crystal
	Medium	Medium	Strong	Faint	Strong
Sodium selenate ..	342	415	835	875	842
Potassium selenate ..	340	409	835	875	839
Ammonium selenate	339	410	835	872	..
Magnesium selenate..	338	412	836	876	840
Thalious selenate	810

3. Characteristic Frequencies of SeO_4 .

As will be clear from Table I, in solution, all the four selenates give identical Raman spectra, evidently characteristic of the SeO_4 ion. Four lines appear in all, one very strong, corresponding to a shift of 835 cm.^{-1} , and one very faint at 875 cm.^{-1} and two others of medium intensity at 345 and 415 cm.^{-1} respectively. The spectrum bears a strong resemblance to that of SO_4 solutions on the one hand, and of the tetrahalides like CCl_4 , SiCl_4 , etc., on the other. Presumably like these compounds, SeO_4 also has a tetrahedral structure, the four O atoms forming the corners of a regular tetrahedron, with the Se atom in the centre. The four Raman frequencies would then correspond to the four fundamental modes of vibration dynamically possible for such a tetrahedral model. The strong line corresponding to the shift 835 cm.^{-1} is evidently due to the totally symmetrical vibration of the tetrahedral model. This frequency is inactive in the infra-red spectrum.

The theory of oscillations of a tetrahedral molecule, of the type AX_4 , has been worked out in detail by Dennison and others, and we shall quote here only the final expressions obtained by them for the fundamental frequencies.⁴

$$n_1^2 = \frac{f}{m} + \frac{4f'}{m} \quad (1)$$

⁴ See K. W. F. Kohlrausch, *Der Raman-Effekt*, 213.

$$n_2^2 = \frac{f'}{m} + \frac{P}{m} \quad (2)$$

$$n_3^2 + n_4^2 = 2P \frac{3M + 16m}{3mM} + \frac{2f'}{m} + f \frac{4m + 3M}{3mM} \quad (3)$$

$$n_3^2 n_4^2 = \frac{2(4m + M)}{3Mm^2} [5Pf + 8P(f' - P) + f'f] \quad (4)$$

where f , f' and P are arbitrary constants that enter in the potential energy function of the molecule; m and M are the masses of the O atom and the Se atom respectively, and

$$n_i = 2\pi c\nu_i, \quad i = 1, 2, 3, 4;$$

the four ν 's give the wave numbers corresponding to the four fundamental frequencies. The constant f represents the force between Se and O and f' the force between any two O atoms.

If the four ν 's and therefore the n 's are known, the binding forces f and f' can readily be calculated by using the above equations. Thus, for example, eliminating f and P between the equations (1), (2) and (3), we get

$$n_3^2 + n_4^2 - \frac{4m + 3M}{3M} n_1^2 - \frac{32m + 6M}{3M} n_2^2 = - \frac{16m + 4M}{mM} f',$$

from which we can calculate f' . With this value in (1) we get f , and in (2) we get P .

The four fundamental frequencies of SeO_4 and the values of f , f' and P calculated therefrom are given in Table II. The corresponding data for the SO_4 ion are also given for comparison.

TABLE II.

Ion	Fundamental frequencies in cm^{-1}				$f \times 10^{-5}$	$f' \times 10^{-5}$	$P \times 10^{-5}$
	ν_1	ν_2	ν_3	ν_4			
SeO_4^{--} ..	835	342	875	415	4.22	0.59	0.51
SO_4^{--} ..	983	447	1115	623	4.57	1.14	0.74

The forces f and f' are of the same order of magnitude for both the ions, the values for SO_4 being slightly greater, probably due to the slightly smaller dimensions of the SO_4 ion as compared with those of the SeO_4 ion. The Se atom being much heavier than the S atom all the frequencies of SeO_4 are naturally smaller than the corresponding frequencies of SO_4 .

4. Heat of Dissociation.

If we take νc to be the oscillation frequency corresponding to the Se-O bond, we may write

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{f}{\mu}}, \quad \text{where } \mu = \frac{mM}{m + M}.$$

Substituting the proper values for f and μ , we get for the Se-O bond

$$\nu = 733 \text{ cm.}^{-1}$$

Calculating in the same manner, we obtain for the S-O bond

$$\nu = 852 \text{ cm.}^{-1}$$

The corresponding heats of dissociation can be calculated in the following manner. For this purpose we may take the C-C binding in benzene, for which $\nu = 990 \text{ cm.}^{-1}$ which is known to correspond to a heat of dissociation of 71 K calories per mol. If we assume that the binding force f is proportional to the heat of dissociation D , we have the relations

$$\frac{D}{D'} = \frac{f}{f'} = \frac{\nu^2}{\nu'^2} \cdot \frac{\mu}{\mu'},$$

where ν , μ and D refer to the C-C bond, and ν' , μ' and D' to the Se-O bond.

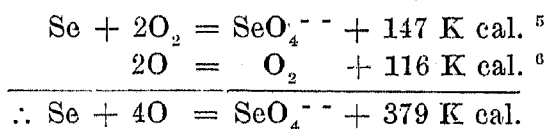
$$\begin{aligned} \therefore D' &= \frac{\nu'^2}{\nu^2} \cdot \frac{\mu'}{\mu} \cdot D \\ &= \frac{733^2}{990^2} \times \frac{79.2 \times 16}{95.2 \times 6} \times 71 = 86 \text{ K cal. per mol.} \end{aligned}$$

A similar calculation for S-O gives

$$D' = \frac{852^2}{990^2} \times \frac{32 \times 16}{48 \times 6} \times 71 = 93 \text{ K cal. per mol.}$$

5. Comparison with Thermochemical Data.

That the above values of the heats of dissociation of the Se-O and the S-O bonds are of the proper magnitude can be seen from thermochemical data. For the Se-O bond we have the following thermochemical relations:—



If we consider the dissociation of SeO_4 as equivalent approximately to four times the heat of dissociation corresponding to the Se-O bond, we get for the latter $379/4 = 95$ K calories, in agreement with 86 K calories obtained from the Raman frequencies.

⁵ *International Critical Tables*, 5, 178.

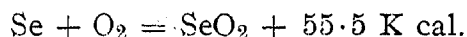
⁶ Frerichs (*Phys. Rev.*, 1931, 37, 903) from spectroscopic data, obtains for heat of dissociation of O_2 into two neutral atoms the value 117.3 K cal., while V. Henri from the predissociation limit of NO_2 gives the value 114.6 K cal. The value 116 adopted here is the mean of these two values.

Similarly, from the heat of formation of SeO_3 , *viz.*,



we obtain for the heat of dissociation corresponding to the Se-O bond 99 K calories.

Again the relation



leads to a value of 86 K calories for Se-O. These values are collected together in Table III, along with similar values for the heat of dissociation of the S-O bond. While it is recognised that this method of comparing the results for the heats of dissociation is only approximate, it is interesting to find that the values calculated from the Raman spectra are of the proper order of magnitude.

TABLE III.

	Heat of Dissociation in K cal. per mol.	Method.
Se-O bond ..	86	from Raman frequencies
	95	„ SeO_4^{--}
	99	„ SeO_3^{--}
	86	„ SeO_2
S-O bond ..	93	from Raman frequencies
	111	„ SO_4^{--}
	107	„ SO_3^{--}
	97	„ SO_2

6. The Force Constants of SeO_4 according to Nagendra Nath's Formulae.

The dynamical theory of the vibrations of AX_4 molecules of tetrahedral symmetry as worked out by Dennison requires some modifications. While it gives values for the frequencies that are in approximate agreement with the observed frequencies, the deviations are too large to be explained as due to errors in observation. As shown in Section 3, we have in Dennison's treatment four equations connecting only three constants. The values of these constants as determined from the first three equations, when substituted in (4) gives for $n_3 n_4$ a value that differs by about ten per cent. from the observed value. This means a difference of 15 to 20 wave numbers in

the observed frequency shifts which is evidently more than what can be allowed for as experimental error.

A different theory has been worked out by Nagendra Nath⁷ in which he assumes four force constants in evaluating the potential energy of the molecule. These correspond to (1) the primary valence force, *i.e.*, between the central atom A and the corner atom X, (2) the directed valence force arising from the directional properties of the valence bonds, (3) the force of repulsion between any two corner atoms XX, and (4) the "intra-valence" force. The values of these four force constants respectively denoted by K, K', K'' and K''' for SeO₄ and SO₄ as calculated from the four observed frequencies are given in Table IV where *l* represents the length of the AX bond.

TABLE IV.

		$K \times 10^{-5}$	$K'' \times 10^{-5}$	$\frac{K'}{l^2} \times 10^{-5}$	$\frac{K'''}{l^2} \times 10^{-5}$
SeO ₄	..	5.365	0.304	0.369	-0.102
SO ₄	..	6.113	0.752	0.585	-0.207

7. Crystalline Selenates.

Only a preliminary study has been made in this paper of the Raman spectra for the crystal state. The prominent symmetrical oscillational frequency of the SeO₄ group appears conspicuously in all the crystals. Its value, however, is not constant as in the case of the solutions, but varies from compound to compound. In thalious selenate it has the lowest value, *viz.*, 810 cm.⁻¹ In sodium selenate two new frequencies are noticed at about 1205 and 1350 cm.⁻¹ respectively.

8. Selenic Acid.

The Raman spectrum of a strong aqueous solution of selenic acid was studied and its spectrum was found to be strikingly different from that of the selenates in solution, reminding one of similar differences observed between sulphuric acid and the sulphate solutions. Table V gives the Raman frequencies in the two cases.

⁷ *Indian Jour. Phys.*, 1934, **8**, 581.

TABLE V.

H_2SeO_4	Strong solution	315 (<i>m</i>)	422 (<i>m</i>)	730 (<i>f</i>)	850 (<i>s</i>)	926 (<i>f</i>)	
SeO_4	..	342	415	..	835	875	
H_2SO_4	90%	422 (<i>m</i>)	569 (<i>m</i>)	916 (<i>s</i>)	1038 (<i>f</i>)	1172 (<i>f</i>)	1294 (<i>f</i>)
	10%	432	598	893	978	1046	1200
SO_4	..	447	623	..	983		1115