

RAMAN SPECTRUM OF RUTILE

Polarisation Studies

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1. INTRODUCTION

THE Raman spectrum of rutile was first studied by the author (Narayanan, 1950) and utilising the observed frequencies, a theoretical study of the vibration spectrum of rutile has been made by Dayal (1950) and more recently by Matossi (1951). Dayal assumed that all the six oxygen atoms that surround a titanium atom in rutile are bound by the same force and this has no theoretical justification except one of simplicity. Matossi making no such assumption arrived at the interesting result that two of the oxygen atoms are attached to each Ti atom far more strongly than the other four, indicating that rutile might be regarded as being built of a body-centred arrangement of TiO_2 molecules. He concluded that the spectrum must be considered as one of 'modified coupled TiO_2 molecules'. Consequently TiO_2 (rutile) was found to be 'geometrically a co-ordination compound, dynamically molecular and spectroscopically of a transition type'.

However, the numerical values of the force constants on which the conclusions mentioned above depend, require a correct assignment of the observed Raman frequencies to the several species and for this polarisation data are necessary. Such information, obtained by the author from a study of the polarisation of the three most intense lines and their relative intensities for different orientations of the crystal is given below.

2. EXPERIMENTAL DETAILS AND RESULTS

The specimen of rutile used for the present study was cut and polished in the form of a rectangular parallelepiped (5 mm. \times 5 mm. \times 6 mm.) with two of its faces perpendicular to the optic axis and the other four parallel to it. It was noticed that the faces perpendicular to the optic axis could be polished more easily than the others. Also along the optic axis, which was determined accurately with the help of the interference figures observed with convergent polarised light, there was a very small amount of strain birefringence. The Raman spectrum excited by λ 4358 radiation of a mercury arc

was recorded with the help of a Hilger two-prism spectrograph of high light-gathering power. The scattered light from the crystal passed through a Wollaston double-image prism and the two images were focussed on the slit of the spectrograph with a quartz lens. Using a slit width of 75μ , exposures of the order of 4 days were necessary to record even the intense lines. Also, since the crystal used was small, there was a certain amount of unavoidable continuous spectrum overlaying the Raman lines and this made it impossible to study the polarisation characteristics of the weaker lines.

The depolarisation factors of the three intense lines are listed in Table I. Since the slit width used in the earlier work was comparatively large and there is more than one line in the neighbourhood of 600 cm.^{-1} , the frequency shift given in Table I for Type A_{1g} is slightly different from the value given before (*loc. cit.*) which referred to the position of maximum intensity.

TABLE I

Case	Direction of optic axis	Type	Frequency shift in cm.^{-1}	Experimental Depolarisation			Theoretical Depolarisation		
				I.L. Electric vector along		Unpolarised light	I.L. Electric vector along		Unpolarised light
				OY	OZ		OY	OZ	
I	OZ	A_{1g}	610	-	~ 0.1	0.1	f	0	0
II	OY			-	-	-	f	0	0
III	OX			-	0	0	f	0	0
I	OZ	E_g	236	-	~ 0	0			
II	OY			-	-	.5			
III	OX			-	-	~ 1			
I	OZ	E_g	444	0	∞	1	0	∞	1
II	OY			-	-	~ 1	1	f	1
III	OX			-	∞	∞	∞	∞	∞

Incident light along OX

Scattered light along OY.

The picture taken with the optic axis perpendicular to the plane of scattering and parallel to it (coinciding with the direction of illumination) show a marked difference, the line 610 cm.^{-1} being of very small intensity when the optic axis is perpendicular to the plane of scattering. The spectra corresponding to case I and with polarised incident radiation (vertical and

horizontal) suggest that the line 515 cm.^{-1} has a depolarisation value $\rho > 1$. Further, spectra taken with unpolarised incident radiation and the optic axis along the direction of illumination revealed the existence of a very weak line at about 820 cm.^{-1} . The low frequency Raman line 150 cm.^{-1} was practically absent when the optic axis was perpendicular to the plane of scattering.

3. DISCUSSION

The total intensities and depolarisation factors for different orientations corresponding to the four symmetry types of oscillations allowed in Raman effect for a tetragonal crystal like rutile may easily be written out from a knowledge of the non-vanishing components of the polarisability tensor (Placzek, 1934; Saksena, 1940). Of these only those of types A_{1g} and E_g are given in Table I along with the experimental results.

The most interesting observation of the present study is that the Raman line at 440 cm.^{-1} is not the most intense one as seen in the earlier spectrograms obtained by the author (1950). When the optic axis is along the direction of incidence the line at 610 cm.^{-1} is nearly twice as intense as that at 440 cm.^{-1} . The complete polarisation of this line in case III enables one to identify it as belonging to the type A_{1g} . The large variation in intensity of the line 610 cm.^{-1} arising from the totally symmetric oscillation is in agreement with the known large birefringence of rutile. Similarly the polarisation values of the 440 cm.^{-1} line makes it possible to identify it beyond doubt as arising from the degenerate mode (Type E_g).

But the polarisation values of the broad line at 236 cm.^{-1} in all the cases studied do not coincide with that to be theoretically anticipated for type B_{1g} and as such no definite assignment could be made for it.

In view of these polarisation data and consequent revision of the assignment of the Raman lines, it will be of interest to recalculate the force constants, which will give information concerning the structure of rutile. For this the more general expressions given by Matossi (1951) were employed. The rutile structure is tetragonal with the basis Ti $(000, \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and O $(uuo; \frac{1}{2} + u, \frac{1}{2} - u, \frac{1}{2}; \bar{u}\bar{u}o; \frac{1}{2} - u, \frac{1}{2} + u, \frac{1}{2})$ with $u = .31$; $a = 4.58 \text{ \AA U}$ and $c = 3.73 \text{ \AA U}$. The structure may be pictured in the following manner. The titanium atoms are at the corners and the body centre of the tetragonal unit cell. To each Ti at the corners are attached two oxygen atoms at equal distances along the direction of one of the basal diagonals. To the Ti at the body centre are attached two oxygen atoms at equal distances but in the direction of the other basal diagonal. Now, the system of force constants used by Matossi may be summarised as follows: k_1 (horizontal) Ti—O (5 and 1); k_2 (oblique) Ti—O (5 and 2); k' (horizontal) O—O (4 and 2);

k'' (oblique) O—O (4 and 1); d_1 , the bond bending force in the horizontal plane O—Ti— (1—5—3); d_2 similar to d_1 but in vertical plane and d_3 at O (5—4—5'), the numbers within brackets referring to the atoms marked in the paper quoted. However, it was necessary to make some assumptions before the numerical evaluations could be made and so k' and d_3 were put equal to zero. Since it was not possible to determine definitely the Raman line due to the oscillation B_{1g} , d_1 was also set equal to zero and the value of (k_2) which was evaluated using the infra-red active frequency $\omega_6 = 330 \text{ cm.}^{-1}$ (extraordinary ray) for the type A_{2u} , will thus be the upper limit. It can be easily seen that this approximation will not affect the magnitude of k_2 much. The frequencies calculated with $k_1 = 2.8 \times 10^5$ dynes/cm., $k_2 = .52 \times 10^5$ dynes/cm. and $k'' = .55 \times 10^5$ dynes/cm. are: $\omega_1 = 610$, $\omega_2 = 685$, $\omega_3 = 173$, $\omega_4 = 895$, $\omega_5 = 444$, $\omega_6 = 330$, $\omega_8 = 536$ and $\omega_9 = 200 \text{ cm.}^{-1}$. The value of the force constant d_2 may be adjusted to account satisfactorily the position of the infra-red maxima (ordinary ray). The main result of the above interpretation, which cannot be attributed to the simplifications, is the great difference between k_1 and k_2 and this can be taken as indicating the molecular character of rutile.

While the experimentally observed lines at 150 cm.^{-1} and 820 cm.^{-1} may be due to the modes B_{1g} and B_{2g} , we find still a large number of lines which have to be attributed to the octaves or combinations of the fundamental frequencies or to violation of the selection rules for the fundamentals.

In conclusion, the author wishes to express his sincere thanks to Prof. R. S. Krishnan for his help and suggestions.

SUMMARY

A study of the intensity and polarisation of the Raman lines of rutile has been made for different orientations of the crystal. The polarisation data show that the Raman line 610 cm.^{-1} belongs to the totally symmetric mode A_{1g} and the line 444 cm.^{-1} to the degenerate mode E_g . A calculation of the numerical values of the force constants for rutile taking into account this reassignment reveals that out of the six oxygen atoms which surround any titanium atom, two are bound to it much more strongly than the others.

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