

# RAMAN SPECTRUM OF RUTILE ( $\text{TiO}_2$ )

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## 1. INTRODUCTION

RUTILE has a simple structure characteristic of compounds of the type  $\text{AB}_2$ , in which the A atom has a co-ordination number 6, and a study of its Raman spectrum is therefore of special interest. A large boule of synthetic rutile and a smaller cut stone were placed at the disposal of the author by Professor C. V. Raman and enabled a study of its Raman spectrum to be made. The results are described below.

## 2. EXPERIMENTAL RESULTS

As the specimen used in the present investigation was coloured slightly yellow, only the visible radiations of the mercury arc could be used for exciting the Raman spectrum. However, as the refractive index of rutile is known to be unusually high (2.9), it is natural to expect the scattering to be very intense. A Hilger two prism spectrograph of high light gathering power and with a dispersion of  $140 \text{ cm.}^{-1}$  in the  $\lambda 4358$  region was used and the slit-width employed in the preliminary exposures was 0.15 mm. It was noticed that even with a much smaller (cut) specimen, exposures of the order of 8 hours were sufficient to bring out the main features of the spectrum, while with the larger specimen which was in the form of a boule  $1\frac{1}{4}$ " long intense pictures were obtained in 3 days. The frequency shifts and the nature of the Raman lines observed are given in Table I.

The Raman lines excited by  $\lambda 5461$  line of mercury were of considerably greater intensity, owing to the slightly yellowish colouration of the crystal. But as a spectrograph with a large dispersion in the green region was not available, the author was unable to make use of the above observation.

The Raman spectrum of rutile reveals some very interesting features. In addition to the five intense lines at 236, 440, 515, 589 and  $650 \text{ cm.}^{-1}$ , there are two broad bands  $350-420 \text{ cm.}^{-1}$  and  $1,000-1,200 \text{ cm.}^{-1}$ . The former shows some structure. In the reproduced microphotometer record (see Fig. 1), the lines appear to be unusually broad, mainly due to the width of the slit employed in recording them.

TABLE I

Mode	Frequency shift in cm. <sup>-1</sup>	Intensity	Nature of the line
-	150	0	-
B <sub>1g</sub>	236	5	Broad and diffuse
A <sub>2u</sub>	(Infra-red) 333		
E <sub>g</sub>	300-440	6	Broad
A <sub>1g</sub>	440	10	Sharp
-	515	3	..
B <sub>2g</sub>	589	7	..
-	650	3	..
-	1,000-1,200	1	-

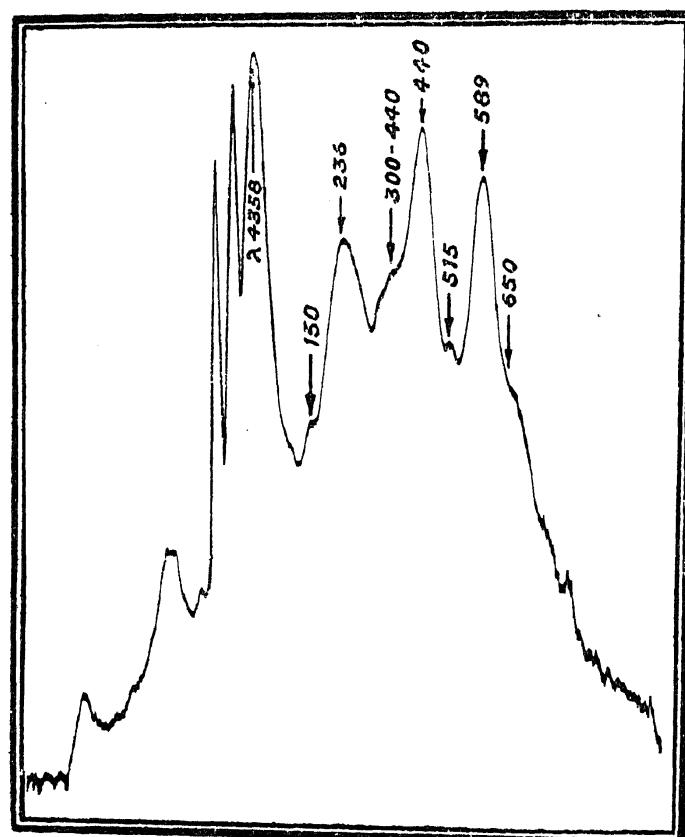


FIG. 1. Microphotometer Curve of the Raman Spectrum of Rutile.

## 3. DISCUSSION

The crystal structure of rutile, which is isomorphous with casseterite ( $SnO_2$ ) is essentially very simple and has been determined by L. Vegard (1916). It is based on a tetragonal lattice with the space group  $D_{4h}^{14}$  and the unit cell contains 2 molecules. Fig. 2 represents the projection of the unit cell on the basal plane (001). The titanium atoms are at the corners

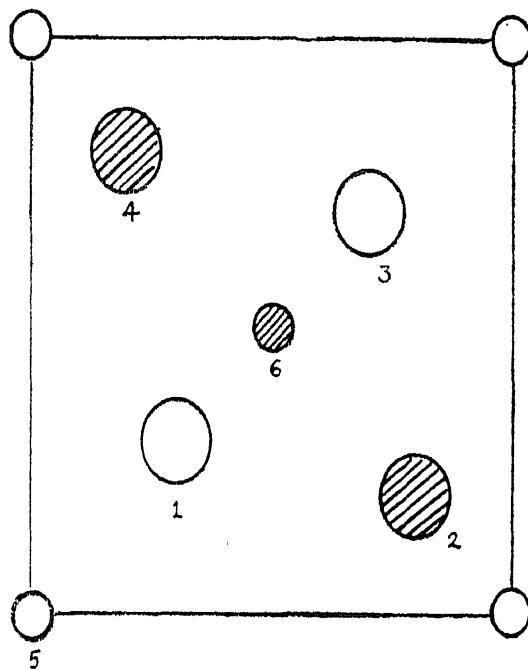


FIG. 2. Raman Spectrum of Rutile

and centres of the cells, while the oxygen atoms lie on the base diagonals and at similar positions half-way up the cell with the co-ordinates given below.

$T_i$  atoms (5, 6) 000;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;

$O$  atoms (1, 2, 3, 4)  $uuo$ ;  $\frac{1}{2} + u, \frac{1}{2} - u, \frac{1}{2}$ ;  $\bar{u}\bar{u}o$ ;  $\frac{1}{2} - u, \frac{1}{2} + u, \frac{1}{2}$ ;

with the parameter  $u = 0.31$

The operations of the group may be expressed as follows:

$E$  (Identity)

$2C_4^s$   $\begin{cases} (4123) (65) \\ (1432) (56) \end{cases}$

$C_2''$  (13) (24) (5) (6)

$2C_2^s$   $\begin{cases} (12) (34) (56) \\ (14) (23) (56) \end{cases}$

$2C_2'$   $\begin{cases} (13) (5) (56) \\ (5) (1) (6) (3) (24) \end{cases}$

$\sigma_h$	(1) (2) (3) (4) (5) (6)
$2\sigma^g$	{(56) (12) (34) {(56) (14) (23)}
$2\sigma_v'$	{(5) (6) (4) (2) (13) {(5) (6) (1) (3) (24)}
$2S_4$	{(1432) (56) {(4132) (65)}
i	(5) (6) (24) (13)

By the application of the group theoretical methods to the Bravais cell of smallest size, it is possible to obtain useful information concerning the (3  $p - 3$ ) internal oscillations of the  $p$  non-equivalent atoms in the unit cell. The character table and other relevant features are given in Table II.

TABLE II

$D_{4h}$	E	$2C_4$	$C_2''$	$2C_2$	$2C_2'$	$\sigma_h$	$2\sigma_v$	$2\sigma_v'$	$2S_4$	i	$n_i$	T	$n_i'$	Raman	Infra-red	
$A_{1g}$	..	+1	+1	+1	+1	+1	+1	+1	+1	+1	1	0	1	p	f	
$A_{1u}$	..	+1	+1	+1	+1	-1	-1	-1	-1	-1	0	0	0	-	-	
$A_{2g}$	..	+1	+1	-1	-1	-1	-1	-1	+1	+1	1	0	1	f	f	
$A_{2u}$	..	+1	+1	+1	-1	-1	-1	+1	+1	-1	2	1	1	f	$M_z$	
$B_{1g}$	..	+1	-1	+1	+1	-1	+1	+1	-1	-1	+1	1	0	1	p	f
$B_{1u}$	..	+1	-1	+1	+1	-1	-1	-1	+1	-1	2	0	2	f	f	
$B_{2g}$	..	+1	-1	+1	-1	+1	+1	-1	+1	-1	+1	1	0	1	p	f
$B_{2u}$	..	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	0	0	0	f	f
$E_g$	..	+2	0	-2	0	0	2	0	0	0	+2	1	0	1	p	f
$E_u$	..	+2	0	-2	0	0	+2	0	0	-2	4	1	3	f	$M_x$	
$U_x$	..	6	0	2	0	4	6	0	4	0	2					
$\chi_p(R)$	18	0	-2	0	-8	6	0	8	0	-6						

We see from the table that the 15 modes fall under 8 representations of which 4 are allowed in the Raman effect and 4 in the infra-red. As a centre of inversion is one of the elements in the group, the infra-red maxima and Raman shifts are complementary. Modes  $A_{1g}$  and  $B_{2g}$  are both symmetric with respect to the centre of symmetry and differ in respect to their behaviour towards the fourfold screw axis. In both these modes, the Ti

atoms are at rest. In the symmetric vibration, atoms 1 and 3 move towards each other and 2 and 4 move out, while in the other mode the two pairs move in or out in phase. Obviously we can expect the vibration  $B_{2g}$  to have the higher frequency.

The third non-degenerate vibration allowed in Raman effect is one in which the Ti atoms are at rest and the O atoms move tangentially with respect to the bond Ti — O and as such is likely to show a large amount of thermal broadening. The broad line at  $230\text{ cm.}^{-1}$  may be assigned to this mode and a study of the spectrum at a low temperature may be expected to confirm this assignment. Table I gives the assignment of the Raman lines from a consideration of their activity in the infra-red and Raman effect and their relative intensities.

The infra-red rest-strahlen maxima, as reported by Liebisch and H. Rubens, are:

Ordinary ray	$14\cdot5\mu$	$16\mu$	$18\cdot5\mu$	$39\mu$
Extra-ordinary ray	$16\mu$	$19\cdot3\mu$	$22\cdot2\mu$	$30\mu$

It is believed that the maxima  $16\mu$ ,  $18\cdot5\mu$  and  $19\cdot3\mu$  are due to the degenerate modes  $E_u$  in which the atomic displacements are perpendicular to the C axis, though for a definite assignment of these as well as the maxima at  $14\cdot5\mu$ ,  $39\mu$  and  $22\cdot2\mu$  a theoretical evaluation of the frequencies of vibration is essential. The Raman line at  $515\text{ cm.}^{-1}$  is probably due to the same mode as the infra-red maxima in the neighbourhood of  $19\mu$  though according to selection rules, it is not permitted in Raman scattering. As in diamond, the enormous scattering power results in the appearance of the second-order spectrum as a broad band from  $1,000$ – $1,200\text{ cm.}^{-1}$ .

The author is indebted to Professor C. V. Raman for a loan of the specimens used in this investigation and to Professor R. S. Krishnan for his guidance in the course of the work.

#### SUMMARY

The Raman spectrum of rutile ( $TiO_2$ ) has been recorded using the visible radiations of the mercury arc. The 8 observed Raman lines have been partially explained on the basis of an elementary group-theoretical analysis.

#### REFERENCES