THE RAMAN SPECTRUM OF RUTILE

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1. Introduction

Titanium dioxide occurs in three different crystalline modifications, *viz.*, rutile, brookite and anatase. Rutile is uniaxial and exhibits a remarkably high refraction and birefringence. The study of its Raman spectrum is of much interest especially in view of the relative simplicity of its crystal structure. The Raman effect in rutile was first reported by Narayanan (1950). Dayal (1950) and Matossi (1951) have discussed the theoretical aspects of the subject in the light of the experimental facts. The polarisation characters of the Raman lines and their identification had been dealt with by Narayanan in another paper (1953).

The theoretical and experimental investigations cited above have not resulted in an unambiguous identification of all the fundamental Raman frequencies of the crystal. The conclusions of the different authors are also in conflict with each other and hence a re-examination of the subject appeared to be called for. The Raman spectrum of rutile observed at room temperature exhibits several broad and diffuse bands, the number of which much exceeds that theoretically expected. It therefore appeared to be desirable to study the Raman effect in rutile at room temperature as well as at the temperature of liquid air. The sharpening of the Raman frequencies to be expected at the low temperature is actually observed and this circumstance is of assistance in the interpretation of the results.

2. The Crystal Structure of Rutile

Rutile belongs to the space-group D_{4h}^{14} of the tetragonal system and contains two TiO_2 groups per unit cell. The titanium atoms are situated at the corners and body-centres of the tetragonal lattice, the two non-equivalent titaniums being those at the corner and the body-centre. The oxygen atoms are so arranged that it is possible to identify a linear symmetrical TiO_2

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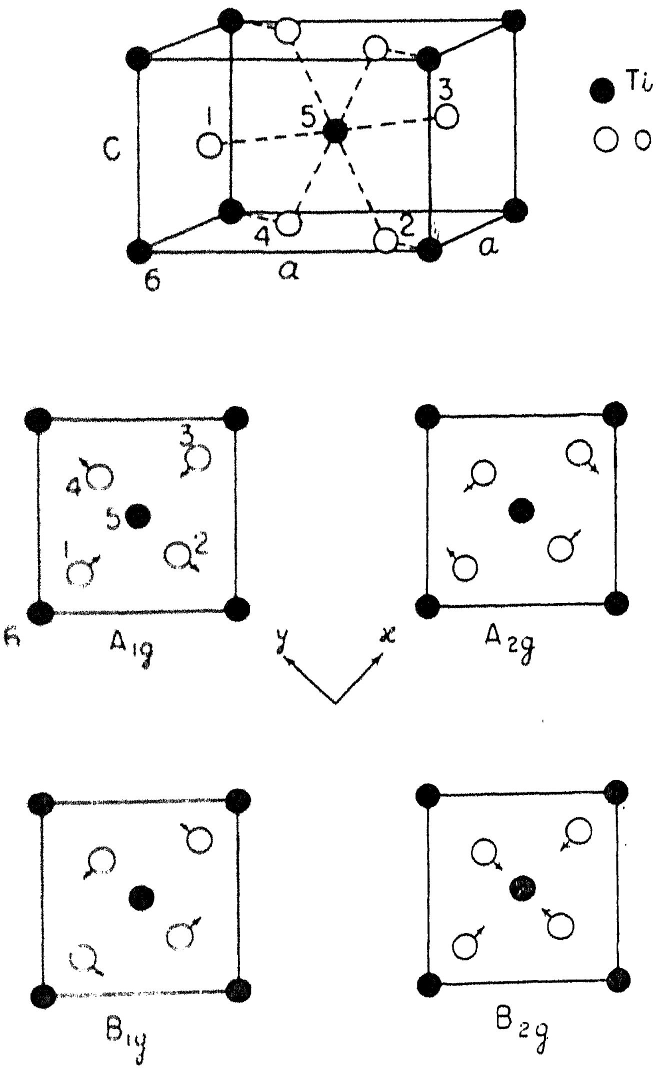
group at each corner and body-centre of the lattice; the two non-equivalent TiO_2 groups lie on the two diagonals perpendicular to each other and passing respectively through the corner and the body-centre. In effect, each titanium atom has as first neighbours six oxygen atoms which are approximately octahedrally co-ordinated around it. Particular mention may be made here of the fact that the two Ti–O distances of each of the linear TiO_2 groups lying perpendicular to the fourfold axis are actually slightly greater than the four other Ti–O distances which are inclined to the fourfold axis. The following are the parameters of the structure of rutile.

$a = 4\cdot594$; $c = 2\cdot959$ A.U. The titaniums are at (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, their site symmetry being D_{2h}. The oxygens are at $\pm(x, x, 0)$ and $\pm(\frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2})$ with $x = 0\cdot306$, the site symmetry of the oxygens being C_{2v}. The axes of reference here are of course the three orthogonal crystal axes.



TEXT-FIG. 1. The structure and some of the modes of vibration of rutile symmetric with respect to the centre of inversion.

3. THE DYNAMICS OF THE RUTILE LATTICE

TABLE I

D_{4h}^{14}	n_i	T	n_i'	Activity	
				R.E.	I.R.
A_{1g}	1	0	1	p	f
A_{2g}	1	0	1	f	f
B_{1g}	1	0	1	p	f
B_{2g}	1	0	1	p	f
E_g	1	0	1	p	f
A_{1u}	0	0	0	f	f
A_{2u}	2	1	1	f	p (M_z)
B_{1u}	2	0	2	f	f
B_{2u}	0	0	0	f	f
E_u	4	1	3	f	p (M_x, M_y)

n_i: total number of vibrations including pure translations.

T: pure translations.

n'_i: total number of vibrations excluding pure translations.

R.E.: Raman effect. I.R.: Infra-red. p: permitted; f: forbidden; M_x, M_y, M_z represent the directions of the oscillatory dipole moments.

Table I shows the selection rules and the number of vibrations under each one of the different species. The different normal modes of vibration can be grouped into two sets, *viz.*, symmetric and antisymmetric with respect to the centre of symmetry. Amongst the former there are four species A_{1g}, B_{1g}, B_{2g} and E_g; under each of these there is only one vibration and these four are the theoretically permitted Raman-active fundamentals. In the antisymmetric class there is one normal mode under the species A_{2u} which should be active in the infra-red absorption of the extraordinary ray; besides this there occur three other normal modes of the doubly degenerate species E_u which should be active in the infra-red absorption of the ordinary ray. The vibrations appearing under A_{2g} and B_{1u} are inactive both in Raman effect and infra-red absorption.

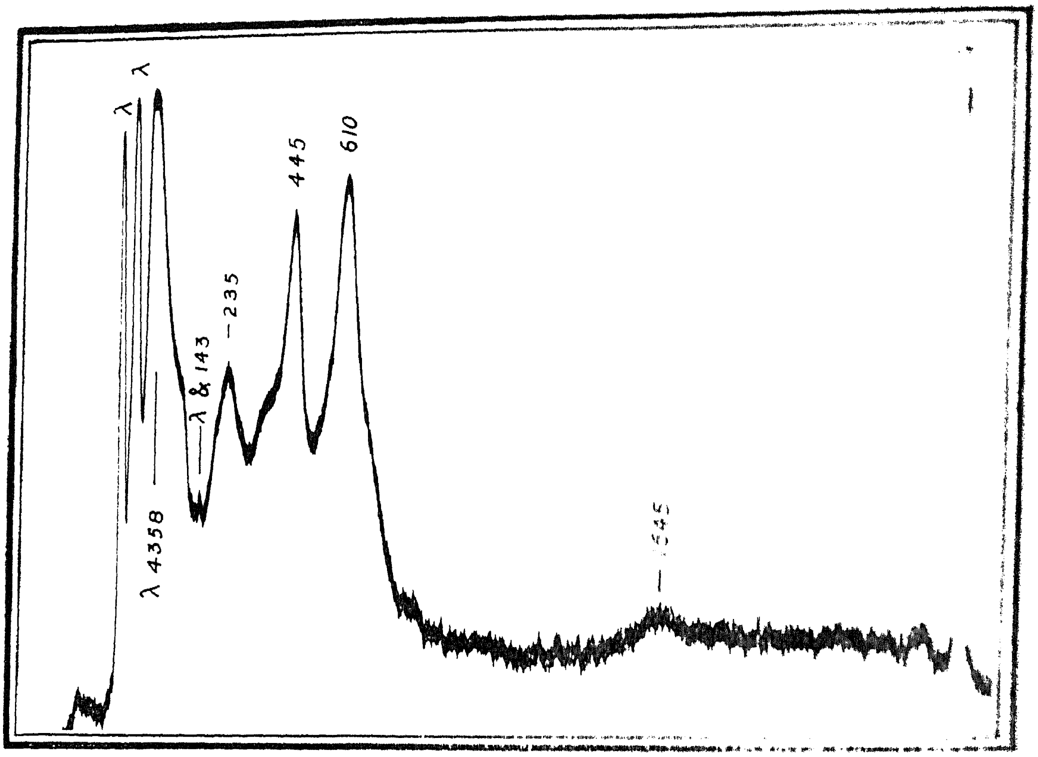
The symmetry co-ordinates of the different modes can be derived by standard procedure. The species referred to by Matossi as B_{2u} in his paper is denoted here by B_{1u} so as to be in conformity with the notation adopted by Wilson in his treatise on 'Molecular Vibrations'. The following are the symmetry co-ordinates for the vibrations of the different species.

ω_1:	A_{1g}:	$x_1 = -y_2 = -x_3 = y_4$
ω_2:	A_{2g}:	$y_1 = x_2 = -y_3 = -x_4$
ω_3:	B_{1g}:	$y_1 = x_2 = y_3 = -x_4$
ω_4:	B_{2g}:	$x_1 = y_2 = x_3 = y_4$
ω_5:	E_g:	$z_1 = z_2 = z_3 = z_4$
or		$z_1 = z_2 = z_3 = z_4$
ω_6:	A_{2u}:	$z_1 = z_2 = z_3 = z_4;\ z_5 = z_6$
		with the condition $Mz_5 + 2mz_1 = 0$
ω_8 & ω_9:	B_{1u}:	$z_1 = z_2 = z_3 = -z_4;\ z_5 = -z_6$
ω_{10}, ω_{11} & ω_{12}:	E_u	$x_1 = y_2 = x_3 = y_4;$
		$y_1 = x_2 = y_3 = x_4;$
		$x_5 = y_6;\ y_5 = x_6$
or		$x_1 = y_2 = x_3 = -y_4;$
		$y_1 = x_2 = y_3 = -x_4;$
		$x_5 = y_6;\ y_5 = -x_6$
		with the condition
		$2m(x_1 + x_2) + M(x_5 + x_6) = 0.$

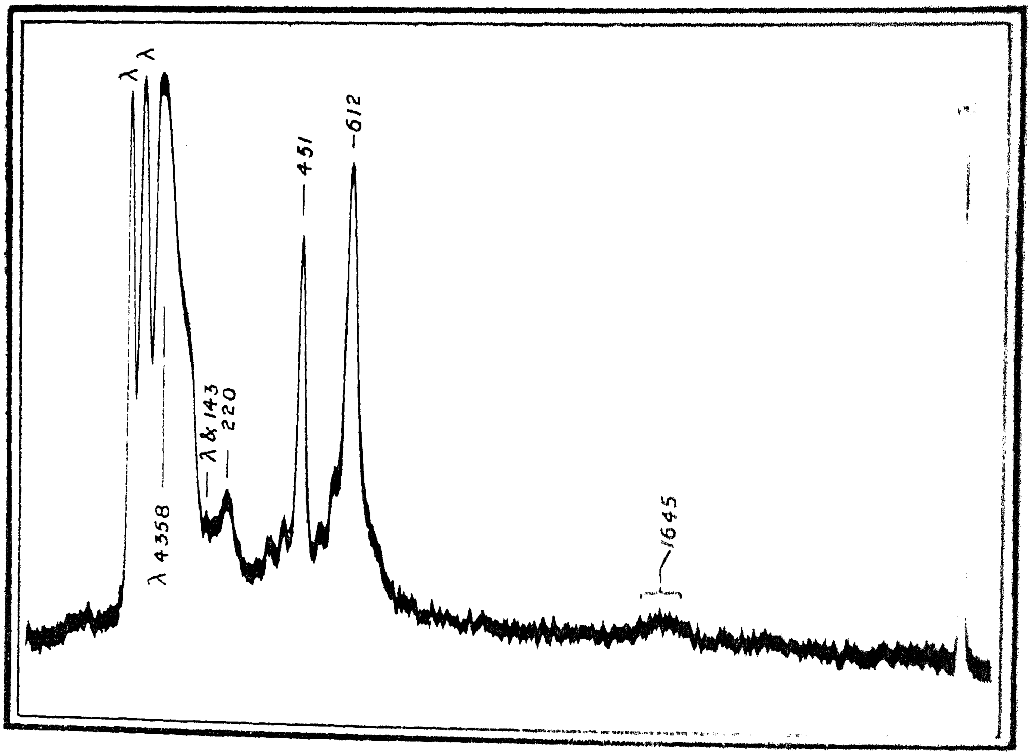
4. Experimental Results and Discussion

The Raman spectra were recorded with the aid of two instruments, one a large aperture (f/4·5) two-prism Huet glass spectrograph and the other a Hilger medium glass spectrograph of slightly higher dispersion. A synthetic specimen of rutile in the form of a boule of length 3 cm. and diameter 2 cm. was used to obtain the spectra; only the λ 4358 radiation of the mercury arc could be used to excite the Raman effect as the crystal was pale yellow in colour and was strongly absorbing even in the near ultra-violet region of the spectrum. With slit widths of about 0·075 mm. exposures of the order of 50 hours were given to obtain intense records of the spectrum.

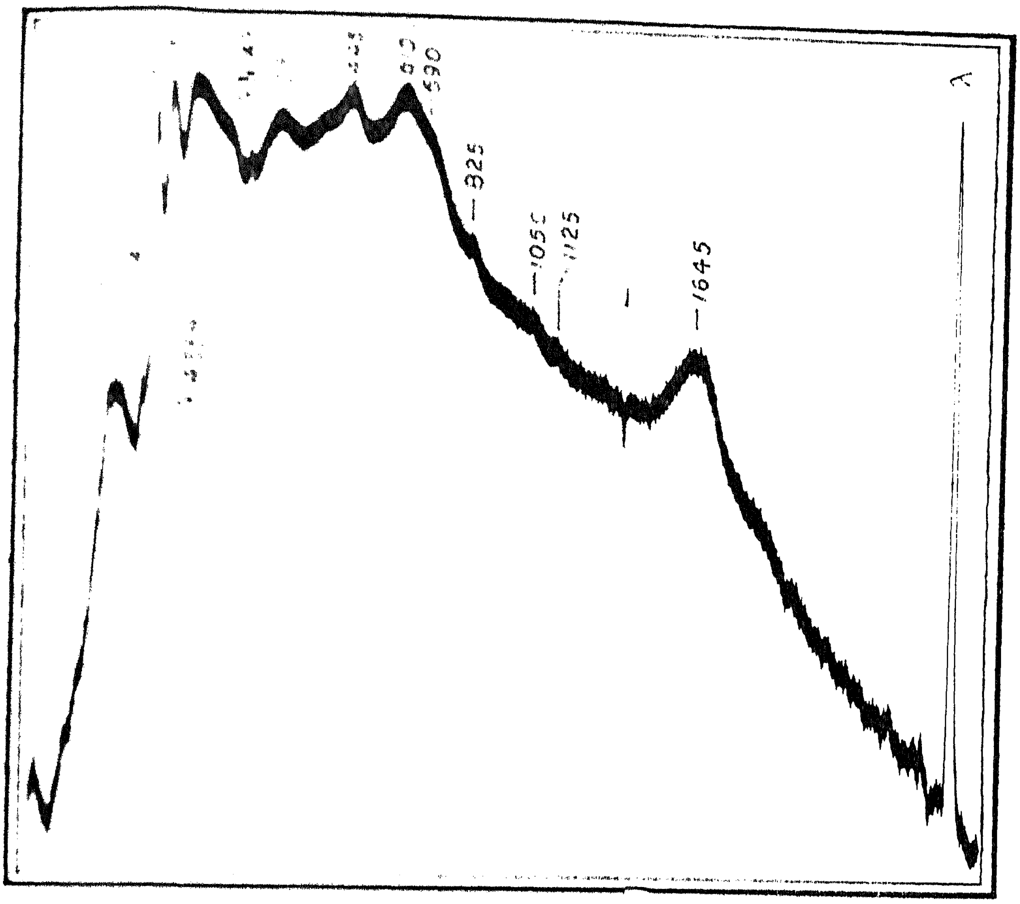
For recording the spectrum at the liquid air temperature a demountable Dewar flask was constructed. The flask consisted of two parts, one an inner vessel of brass to hold the liquid air and the other an outer jacket of glass which was silvered inside; the two vessels were provided with flanges at their upper ends and to get a good vacuum-tight joint between them at the low temperature, silicone DC4 grease proved to be quite useful. A copper block was attached to the lower end of the inner vessel and the crystal was



TEXT-FIG. 2. Microphotometer record of the Raman spectrum of rutile recorded at room temperature.



TEXT-FIG. 3. Microphotometer record of the Raman spectrum of rutile recorded at liquid air temperature.



TEXT FIG. 4. Microphotometer record of a heavily exposed spectrogram exhibiting the weaker Raman lines of rutile at room temperature.

embedded in the copper block with Wood's alloy to secure good thermal contact. The space between the inner vessel and the outer glass jacket was kept continuously evacuated. The outer glass vessel was provided at its lower end with two windows respectively for the entry of the exciting radiations and for the exit of the transversely scattered light.

Plate XXII accompanying the text and the microphotometer records produced in the Text-Figs. 2, 3 and 4 illustrate the different features of the Raman spectrum of rutile. The two very intense Raman lines of shifts 445 and 610 cm.$^{-1}$ constitute the prominent features manifested by even moderately exposed spectrograms. Under prolonged exposures, there appear several other Raman lines of shifts respectively 143 (m), 235 (st), 690 (w), 825 (w), 1050 (w), 1125 (w) and 1645 (w) cm.$^{-1}$ Of these the frequency shifts at 143 and 825 cm.$^{-1}$ are comparatively sharp and the shifts at 235 and 1645 cm.$^{-1}$ are quite broad and diffuse. The spectrum recorded at liquid air temperature exhibits a pronounced sharpening of the lines as may be clearly noticed in the case of the two prominent lines whose shifts at the low temperature are respectively 451 and 612 cm.$^{-1}$ The broad line at 235 cm.$^{-1}$ appears to be diminished in its intensity relatively to the other Raman shifts, and in addition, surprisingly enough, the value of this frequency shift at the low temperature is definitely lower than the room temperature value by about fifteen wave numbers.

The two frequency shifts of 445 cm.$^{-1}$ and 610 cm.$^{-1}$ which are very intense and which appear quite sharp and strong at low temperature obviously represent two of the four theoretically permitted Raman-active fundamentals. In fact, the polarisation studies undertaken by Narayanan definitely show that the frequency shift 610 cm.$^{-1}$ belongs to the totally symmetric species A_{1g} and the other one of shift 445 cm.$^{-1}$ belongs to the doubly degenerate species E_g.

We now proceed to identify the other two Raman-active fundamentals belonging to the species B_{1g} and B_{2g} and also furnish an explanation for the other observed features. From an inspection of the diagrams representing the Raman-active modes A_{1g}, B_{1g} and B_{2g} shown in Fig. 1 in the text it may be noticed that the vibrational frequency of the mode B_{1g} should be extremely low in view of the fact that the movements of *all* the oxygens surrounding any titanium are all strictly perpendicular to the bonds and involve no changes in the Ti-O bond-lengths. (The changes in the O–O distances are also quite small.) On the other hand, in the case of the mode B_{2g} all the oxygens move *simultaneously* towards or away from the central titanium. These movements involve changes in the Ti-O bond-lengths and hence it is obvious that the frequency of this mode should be quite high. The only Raman lines observed in the very low frequency region are the two shifts 235 cm.$^{-1}$ and 143 cm.$^{-1}$ Of these the frequency shift at 143 cm.$^{-1}$ is sharp even at room temperature as can be clearly seen from its appearance on the anti-Stokes side of the record in Text-Fig. 4. On the Stokes side this Raman line is masked by a weak mercury line in this region. The sharpness with which this Raman frequency appears in the spectrum precludes any other explanation for its origin except that of identifying it with the mode B_{1g}.

Matossi has derived detailed expressions for the different normal modes of vibration in rutile in terms of a set of bond-stretching and bond-bending force constants. Without making any approximations whatever regarding the magnitudes of the forces, it may be seen from his paper that there exist the following relationships between the frequencies of the different normal modes:

$$\omega_4^2 - \omega_2^2 = \omega_1^2 - \omega_3^2 \tag{1}$$

where ω_1, ω_2, ω_3 and ω_4 represent the circular frequencies of the modes A_{1g}, A_{2g}, B_{1g} and B_{2g} respectively.

$$\frac{\omega_2^2}{\omega_4^2}\left(\frac{\cos\delta \quad \sin\delta}{\cos\delta \quad \sin\delta}\right) = 16\cdot544 \qquad (2)$$

where δ is a constant connected with the parameters of the structure. With the aid of the above two equations it may readily be seen that the values of the frequencies of the modes A_{2g} and B_{2g} can be calculated assuming the values of the frequencies for the modes A_{1g} and B_{1g}. The calculated values for A_{2g} (inactive in both Raman effect and infra-red) and B_{2g} (Raman-active) are respectively 582 and 831 cm.$^{-1}$ The Raman spectrum indeed exhibits a sharp and well defined frequency shift of 825 cm.$^{-1}$ which obviously arises from the normal mode B_{2g}.

From the above calculations it also emerges that the bond-stretching force constant k' between the two oxygen atoms 4 and 1 has a value $4\cdot226 \times 10^4$ dynes/cm. In addition to the relations which we have cited above there exists one another from which it is possible to calculate the frequency of the absorption maximum to be observed in the extraordinary ray, *i.e.*, mode A_{2u}. This relation is obtained by neglecting to a first approximation the bond angle bending force constant d_1 corresponding to the atoms 1, 5 and 3 which are in a line and are comparatively farther apart from each other. This relation is given by

$$m\omega_5^2 - 8k'\cos^2\chi = \omega_6^2\left(\frac{mM}{2m+M}\right)$$

where k' is the constant mentioned above, m and M are respectively the masses of the oxygen and titanium atoms; ω_5 and ω_6 are the circular frequencies corresponding to the modes E_g and A_{2u}; cos χ has a value $= 0\cdot53$. If we assume the observed value of the frequency shift corresponding to the mode E_g (ω_5), *i.e.*, 445 cm.$^{-1}$ the calculated value for A_{2u} emerges as 344 cm.$^{-1}$ in fair agreement with the observed value of 333 cm.$^{-1}$ reported in the literature. This agreement again confirms our identification of the frequency shift 143 cm.$^{-1}$ as arising due to the mode B_{1g}. The other Raman shifts observed are explicable as overtones and combinations of the Raman-active and infra-red-active frequencies as shown in Table II.

It may be mentioned here that the two broad bands observed (in the spectra recorded at room temperature) on the short-wavelength side of the shifts 445 cm.$^{-1}$ and 610 cm.$^{-1}$ have till now hampered the proper identification of the four fundamental Raman frequencies. However, in the present investigation the spectra recorded at the low temperature clearly show them to be the Raman shifts 445 and 610 cm.$^{-1}$ excited by the two satellites of λ4358 and hence these are eliminated from consideration. Obviously at the room temperature, these shifts, because of their considerable width, merge together to give the observed bands.

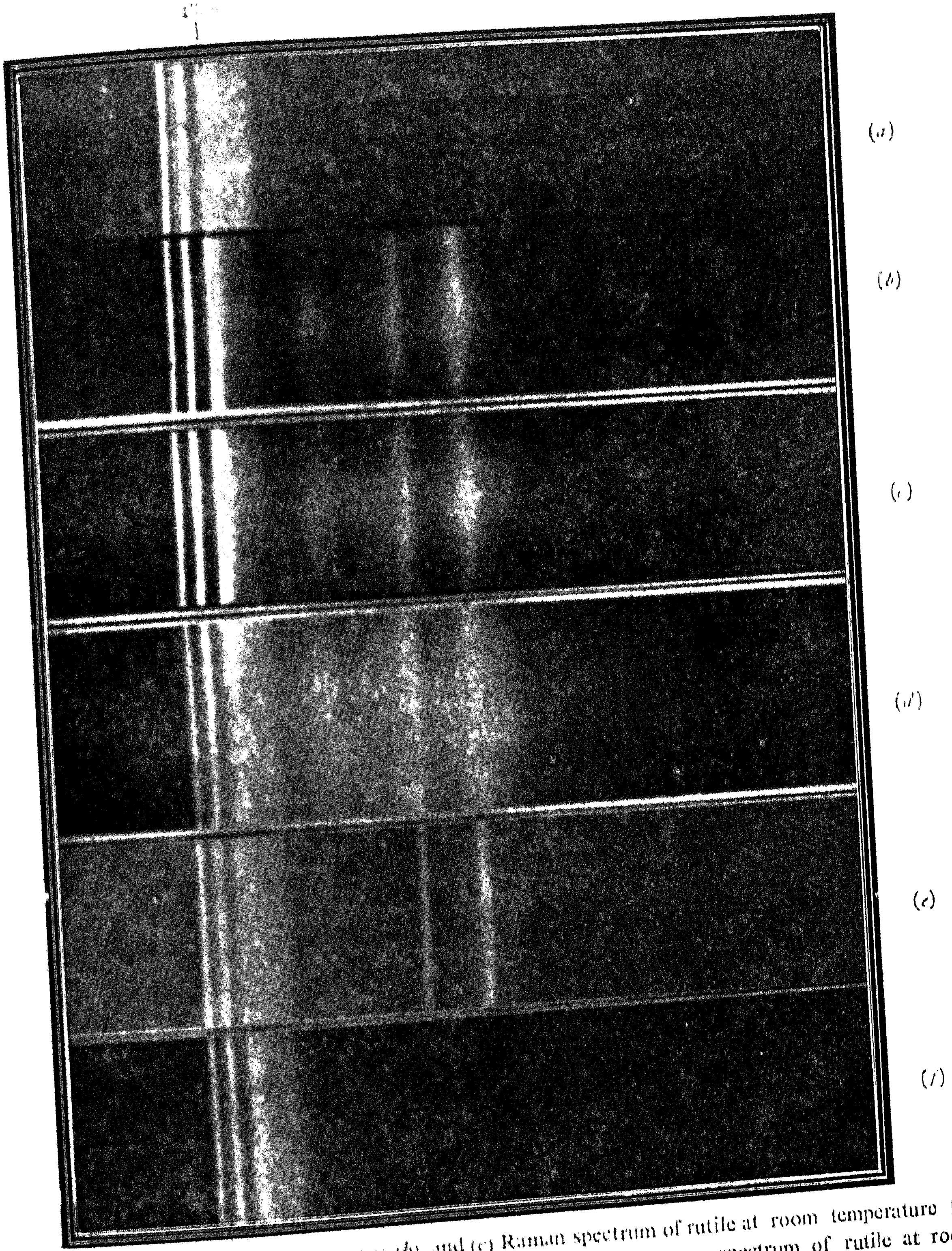
TABLE II

Vibrational frequencies of rutile

Observed value in cm.$^{-1}$	Observed in	Identification	Calculated value in cm.$^{-1}$
143	R.E.	B_{1g}	
235	R.E.	?	
256	I.R.	E_u	
333	I.R.	A_{2u}	344
445	R.E.	E_g	
610	R.E.	A_{1g}	
690	R.E.	$A_{2u}+A_{2u}$	688
825	R.E.	B_{2g}	831
1050	R.E.	$A_{1g}+E_g$	1055
1125	R.E.	$A_{2g}+A_{2g}$?	1164
1645	R.E.	$B_{2g}+B_{2g}$	1650
..	Inactive in both I.R. and R.E.	A_{2g}	[illegible]

Besides the frequencies listed in Table II, studies on the infra-red reflection spectrum of rutile by early investigators (*vide Landolt Bornstein Tables*, 1955, Vol. I, Part IV) have revealed the following maxima, *viz.*, 256, 385, 540, 625 and 690 cm.$^{-1}$ in the ordinary ray and 333 (shown in Table II), 451, 518 and 625 cm.$^{-1}$ in the extraordinary ray. Calculation of frequencies of the infra-red-active species E_u (ordinary ray) and those of the inactive species B_{1u} involves the values of a number of force constants, not all of which could be estimated with the available data. Some of the above maxima, however, may arise by violation of selection rules due to causes to be considered presently.

It is highly probable that the Raman shift of 235 cm.$^{-1}$ arises due to an infra-red-active (but theoretically Raman inactive) doubly degenerate mode of species E_u present in this region—*i.e.*, corresponding to the maximum at 256 cm.$^{-1}$ given above. The origin of the Raman activity of this species in violation of the selection rules can be traced to the fact that there are five



(a) Spectrum of the mercury arc; (b) and (c) Raman spectrum of rutile at room temperature for two different orientations of the crystal; (d) Heavily exposed Raman spectrum of rutile at room temperature; (e) The spectrum of the rutile at liquid air temperature; (f) Spectrum of the mercury arc.

naturally occurring isotopes of titanium of atomic weights 46, 47, 48, 49 and 50 and with relative abundances of 7·95%, 7·75%, 73·45%, 5·51%, 5·34% respectively. Whereas, the selection rules and symmetry modes are derived on the basis that all titaniums are of equal mass, the actual situation is that approximately only three quarters of the total number of titanium atoms are of identical mass, the others varying from 48, the maximum variation being two units either way. It could therefore be expected that the infra-red-active species E_u (which involves also the movements of the titaniums) would become Raman-active, and the low value of the frequency (235 cm.$^{-1}$) is suggestive of this view. In the case of α-quartz, modes of the species B have been observed to be weakly Raman-active in violation of the selection rules and an analogous explanation had been offered by the author (1958). It is also not possible to identify the frequency 235 cm.$^{-1}$ with the mode B_{1g} (instead of 143 cm.$^{-1}$ as has been done), since it leads to a theoretical value of 973 cm.$^{-1}$ for the Raman-active mode B_{2g} and no Raman frequency shift of that value in rutile has been observed.

Finally, it may be pointed out that in the case of mode A_{2g} (Text-Fig. 1) here occur comparatively greater changes in the O–O distances than in the case of the mode B_{1g}, thereby leading to a theoretically calculated value of 582 cm.$^{-1}$ which is greater than that of B_{1g} (143 cm.$^{-1}$), even though both modes are such that no changes in the Ti-O bond-lengths are involved.

In conclusion, the author wishes to express his sincere thanks to Prof. Sir C. V. Raman, F.R.S., N.L., for his kind interest in this investigation.

5. Summary

The Raman spectrum of rutile has been investigated both at room temperature and at the temperature of liquid air. The Raman lines which, at room temperature are quite wide, are observed to sharpen greatly at the low temperature. The different Raman-active fundamentals are identified and the paper also elucidates the several subsidiary features which are observed in spectrograms recorded with prolonged exposures.

6. References

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