On the Positions of the Hydrogen Atoms in the Crystal Structure of Muscovite, as Revealed by the Infra-Red Absorption Study

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Introduction

While studying the near infra-red absorptions of proteins and related substances mounted on thin cleavage pieces of muscovite, the writer's attention was called to the facts that muscovite shows a sharp and strong absorption band at the wave-length 2.75 μ, which was later ascertained to be due to the OH groups in its crystal structure, and that the intensity of this band varies with the direction of the ray in the crystal. In view of the significance of these facts as clue to the positions, hitherto unknown, of the H atoms in muscovite, the writer proceeded to examine in detail how the absorption intensity of the 2.75 μ band varies with the direction of the electric vector of the light that passes through a muscovite crystal. In this paper the results of these experiments are given.

Sample

The sample of muscovite examined is from Tanokami-Yama, Siga Prefecture, and has the following optical constants for D-light: $\alpha=1.559$, $\beta=1.593$, $\gamma=1.598$, $2V=41°$. From this a colorless, transparent cleavage piece, 3 cm. × 3 cm. in size, of uniform thickness (about 18 μ) was taken for observation. Its crystallographic orientation was determined from the X-ray oscillation photograph (Mo Kα) by Mr. H. Mori, through the kindness of Prof. T. Ito, of the Mineralogical Institute, Tokyo University.

Experimental Procedure

The infra-red absorption measurements were made by means of a reflection monochromator with a 60° prism of quartz, in conjunction with the thermocouple and galvanometer system. The infra-red radiation from a heated nichrom wire was reflected by a selenium mirror at the angle of 68° to be polarized,(1) and was passed through the sample, set on a universally rotatable stage with graded circles for reading the angles of rotation.

Absorption Band of Muscovite at 2.75 μ

The percent transmissions of the sample of muscovite were first observed for the light ranging from 2.6 to 3.5 μ in wave-length, and the results shown in Fig. 1, A were obtained.

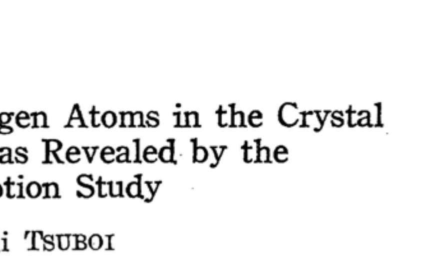

Fig. 1.—A: Percent transmissions of muscovite, 0.018 mm. thick. B: Percent transmissions of artificial mica, 0.3 mm. thick. s: Effective slit width.

Similar observations were made of a cleavage piece, 0.3 mm. thick, of an artificial mica(2) in which F or O substitutes OH in natural muscovite, with the results shown in Fig. 1, B. As may be seen in these figures, while the cleavage piece of natural muscovite, as thin as 18 μ, shows a sharp and strong absorption band at 2.75 μ, the thicker cleavage piece of the OH-free artificial mica shows none. From these observations the band at 2.75 μ may be assigned

(1) Following D. A. Crooks (*Nature*, **160**, 17 (1947)), the efficiency of this setting as a polarizer was judged from the fact that the transmission at 2900 cm.$^{-1}$ of a sample of succinic acid, put in the path of the reflected light, increased from 1 % to 72 % as it was rotated through 90° from the position at which the c axis is parallel to the plane of the selenium mirror.

(2) Prepared by Professor T. Noda ("Kôgyô Buturi-Kagaku," **1**, 103 (1948); **2**, 179 (1948)) and kindly placed at the writer's disposal.

with certainty to the fundamental O-H stretching vibration in crystal of muscovite.

Moreover the absorption band of muscovite is of the same character with that due to the free OH of alcohols in their dilute carbon tetrachloride solutions, in regards to the wave-length of the absorption maximum and the band width. This fact shows that the OH in muscovite is free from the hydrogen bonding, the O-H bond being almost unaffected by the sorrounding atoms in the crystal.

Absorption Intensities in Different Directions of Muscovite

Now that it has become clear that the absorption band at 2.75 μ of muscovite is due to the fundamental O-H stretching vibration, its intensity variation with the direction of the ray must give informations as to the orientations of the O-H bonds in the crystal structure. With the purpose of obtaining such informations, the linearly polarized radiation with the wave-length 2.75 μ[(3)] was passed through the sample of muscovite orientated in various directions, and the percent transmission in each direction was determined. In this experiment the electric vector of polarized light sent to the crystal was always orientated so that it was in the incident plane. The results obtained are shown in Tables 1 and 2 and in Figs. 2 and 3. Throughout this paper, the setting of the crystallographic axes of muscovite as proposed by W. W. Jackson and J. West[(4)] is adopted.

Table 1

Observed Percent Transmissions (m) of Light Sent Perpendicularly to the Cleavage Plane

φ	m, %
90°	43.6
80	44.4
70	45.5
60	47.3
50	49.2
40	51.0
30	52.9
20	53.5
10	54.5
0	55.0
−10	54.4
−20	53.7
−30	52.9
−40	51.5
−50	49.9
−60	47.8
−70	45.5
−80	44.4

φ is the azimuth of the electric vector for the incident light, measured with the crystallographic a axis. It is positive when measured counter-clockwise.

(3) The light used is not strictly monochromatic, but ranges in wave-length 2.69∼2.81 μ, the effective slit width being 0.12 μ, in which the total range of 2.75 μ band is included.

(4) W. W. Jackson and J. West, *Z. Krist.*, **76**, 211 (1930); **85**, 160 (1933).

Table 2

Observed Percent Transmissions (m) of Light Sent Obliquely to the Cleavage Plane

φ	θ	m	φ	θ	m	φ	θ	m
90°	50°	47.0%				−30°	50°	50.5%
	40	46.2	30°	40°	50.0%		40	50.1
	30	45.5		30	50.1		30	50.3
	20	44.4		20	50.8		20	50.6
	10	44.0		10	51.3		10	52.4
	0	43.6		0	52.9		0	52.9
	−10	43.7		−10	54.1		−10	54.1
	−20	44.4		−20	56.4		−20	56.8
	−30	45.2		−30	57.6		−30	59.2
	−40	46.1		−40	61.1		−40	62.0
			0	50	51.4	−60	50	48.4
60	40	49.4		40	52.0		40	47.6
	30	48.0		30	52.2		30	46.6
	20	48.0		20	52.4		20	45.9
	10	47.9		10	53.6		10	46.4
	0	47.8		0	55.0		0	47.3
	−10	48.8		−10	57.0		−10	47.7
	−20	49.8		−20	60.1		−20	48.5
	−30	51.2		−30	64.5		−30	50.2
	−40	52.6		−40	67.5		−40	52.6

φ is the azimuth of the incident plane, measured with the crystallographic a axis. It is positive when measured counter-clockwise. θ is the incident angle of the light. It is positive when measured to the front.

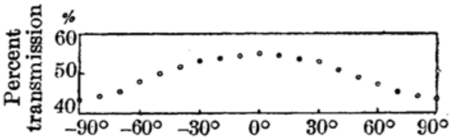

Fig. 2.—Observed percent transmissions of light sent perpendicularly to the cleavage plane of muscovite. As to the meaning of φ, see the note of Table 1.

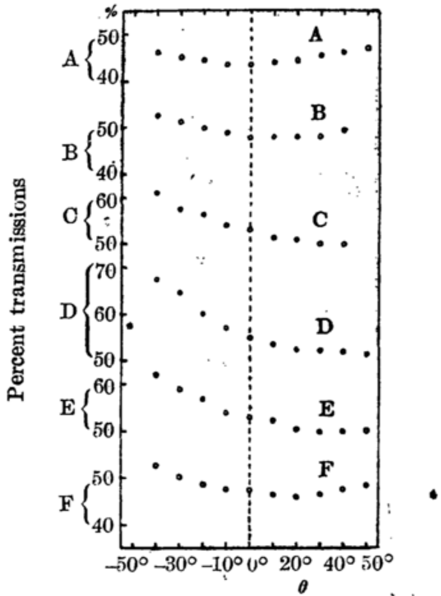

Fig. 3.—Observed percent transmissions of light sent obliquely to the cleavage plane of muscovite. A: $\varphi=90°$, B: $\varphi=60°$, C: $\varphi=30°$, D: $\varphi=0°$, E: $\varphi=-30°$, F: $\varphi=-60°$. As to the meanings of φ and θ, see the notes of Table 2.

In order to know how in the muscovite crystal the absorption coefficient is related to the direction of the electric vector of the passing radiation, the absorption coefficient K in various directions were calculated from the data given above by the following equation, which is based on the Lambert's law:

$$K = \frac{1}{d \sec \chi} \log \left\{ (1-r)^2 \Big/ \frac{I}{I_0} \right\},$$

where d is the thickness of the sample, χ the refracting angle, r the reflection coefficient at each boundary surface of the sample, and I/I_0 the transmittance. The results of the calculations are given in Table 3 and Fig. 4.

Table 3

Relative Absorption Coefficients (for 2.75 μ radiation) in Different Directions in Muscovite (Expressed as $K_b = 1$.)

	φ	ψ	K	φ	ψ	K
From the	90°	24.0°	0.93	60°	24.0°	0.73
		18.5	0.95		18.5	0.75
data in		12.5	0.98		12.5	0.79
		6.3	1.00		6.3	0.81
Table 1:		0	1.00		0	0.84
		−6.3	0.99		−6.3	0.84
$\frac{K_a}{K_b}=0.63$		−12.5	0.98		−12.5	0.84
		−18.5	0.94		−18.5	0.85
		−24.0	0.93		−24.0	0.82
(Cf. remarks		−29.0	0.91			
(5) below)	30°	24.0°	0.50	0°	24.0°	0.37
		18.5	0.56		18.5	0.41
		12.5	0.58		12.5	0.49
		6.3	0.64		6.3	0.56
		0	0.68		0	0.61
		−6.3	0.73		−6.3	0.66
		−12.5	0.76		−12.5	0.70
		−18.5	0.78		−18.5	0.72
		−24.0	0.80		−24.0	0.74
					−29.0	0.76
	−30°	24.0°	0.48	−60°	24.0°	0.73
		18.5	0.53		18.5	0.78
		12.5	0.57		12.5	0.83
		6.3	0.64		6.3	0.85
		0	0.68		0	0.86
		−6.3	0.70		−6.3	0.90
		−12.5	0.76		−12.5	0.92
		−18.5	0.78		−18.5	0.90
		−24.0	0.80		−24.0	0.88
		−29.0	0.79		−29.0	0.86

K_a and K_b are the absorption coefficients of the passing radiations in muscovite whose electric vectors are parallel to the crystallographic axes a and b respectivily. φ is the azimuth of the electric vector of the passing radiation in muscovite. It is positive when measured counter-clockwise, ψ is the angle which the electric vector makes with the cleavage plane. It is positive when measured upward.

Remarks:—In the course of calculating the values of K in Table 3 the following measures were taken:

(1) To find r and χ in the above equation and φ and ψ in the Table 3, the principal refractive indices, α, β and γ, of muscovite for the light of the wave-length 2.75μ must be known. These being unknown, the calculations were made on the assumption that $\alpha = \beta = \gamma = 1.58$. That this assumption does not affect seriously the final results

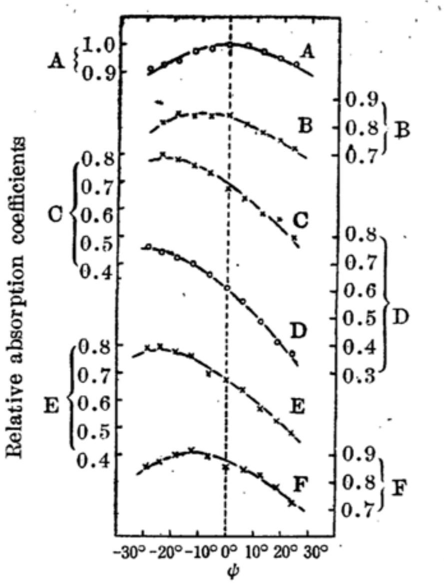

Fig. 4.—Relative absorption coefficients in different directions of muscovite. A: $\varphi=90°$, B: $\varphi=60°$, C: $\varphi=30°$, D: $\varphi=0°$, E: $\varphi=-30°$, F: $\varphi=-60°$. As to the meanings of φ and ψ see the notes of Table 3. The points marked with × represent the values of K, φ and ψ, obtained from calculations including the approximations as remarked in (6) in the text. Those marked with ∘ represent the values obtained without such approximations, the incident planes for the light here concerned containing either one of the crystallographic axes a and b.

aimed at, was ascertained by trials with other assumed values for α, β and γ, such as: (1) $\alpha=1.526$, $\beta=1.544$, $\gamma=1.552$, (2) $\alpha=\beta=\gamma=1.55$, (3) $\alpha=\beta=\gamma=1.61$, etc., all of these trials having given the results not different qualitatively from one another.

(2) In the calculation of r, the absorption index κ (in the formula $n(1-i\kappa)$ expressing the complex refractive index) was neglected, because κ of muscovite is about 0.006 for the light here used, as may be estimated from the Tables 1 and 2, and accordingly κ^2 is negligibly small compared with 1. The values of r were obtained by the Fresnel's formula concerning the reflection of light.

(3) As a test of the applicability of the Lambert's law to the present case, a spectroscopic observation was made of the 2.75 μ absorption band of methanol in dilute carbon tetrachloride solution with the same slit width as that in the experiment with muscovite. This showed that the observed absorbance $\log I_0/I$ is not strictly proportional to the thickness d of the solution, but that the $\log I_0/I$—d curve is somewhat convexly bent. The values of K in Table 3 are those corrected on the basis of this observation, assuming that the deviation of the observed values of $\log I_0/I$ from the Lambert's law is the same for the muscovite and for the methanol. These corrections, though added, are of little importance for the present purpose.

(4) It was not intended to obtain absolute values of K, for the accurate value of d was not known.

(5) The percent transmission, (m) of the light sent perpendicularly to the cleavage plane is given by

$$m = m_a \cos^2\varphi + m_b \sin^2\varphi,$$

where m_a and m_b denote the percent transmissions, respectively of the light with the electric vector parallel to the a axis and of the light with the electric vector parallel to the b axis, into which the incident light is divided after entering muscovite, and φ the angle which the direction of the electric vector of the incident light makes with the a axis. By substituting the values in Table 1 for m and φ in the above formula and by applying the method of least squares, the following values of m_a and m_b were obtained: $m_a = 55.2 \pm 0.1\,\%$, $m_b = 44.4 \pm 0.1\,\%$. From these the ratio of the absorption coefficients, K_a and K_b, were calculated as $K_a/K_b = 0.63$.

(6) The azimuths (φ) of the electric vectors within the crystal for the light sent obliquely to the cleavage plane were taken to be the same with those before entering the crystal, even in the case where the incident plane contains neither the crystallographic axis a nor b. Such approximations are considered to introduce no serious error to the results, because the retardation of the cleavage piece of muscovite for the light under consideration may probably be small compared with its wave-length.

In order to facilitate further discussions the writer here proposes to consider a surface of reference — "absorption coefficient—electric vector surface" or "K-E surface"—which shows the variation of the absorption coefficient in different directions in a crystal. From a point within a crystal, lines are drawn in all directions representing those of the electric vectors of light, and each of these lines is cut so that its length may represent the absorption coefficient for the light concerned, then the surface obtained by the ends of these lines is the K-E surface of the crystal. This is a surface with three extremity axes perpendicular to one another.[5]

The data given in Table 3 and Fig. 4 are indicative of the shape and the orientation of the K-E surface of the muscovite examined. The orientations and the relative lenghts of the three exremity axes of the K-E surface are as follows:

(i) The greatest axis: parallel to the crystallographic axis b. Relative length $=1$.

(ii) The medium axis: orientated at $\varphi = 0°$, $\psi = -30°$, i.e. at 30° from the crystallographic axis a in the acute angle β, in 010 plane.

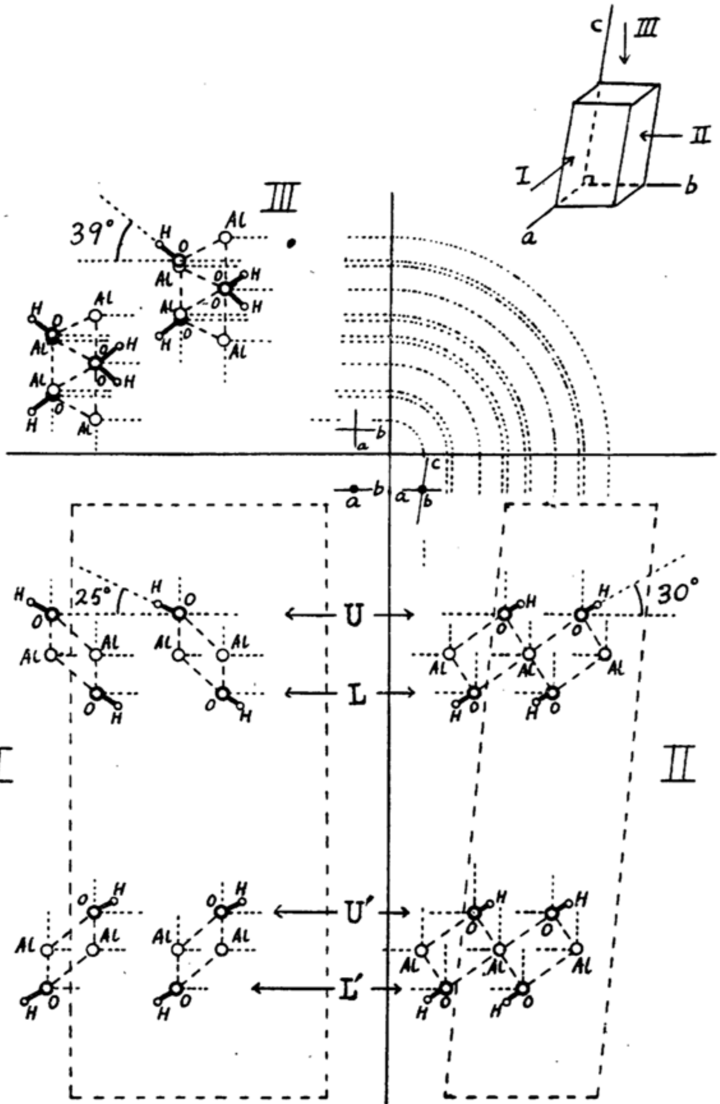

Fig. 5.—Orientations of the OH groups in the unit cell of muscovite. I: Projected on a plane normal to the a axis. II: Projected on 010. III: Projected on a cleavage plane.

(5) Details are to be published elsewhere.

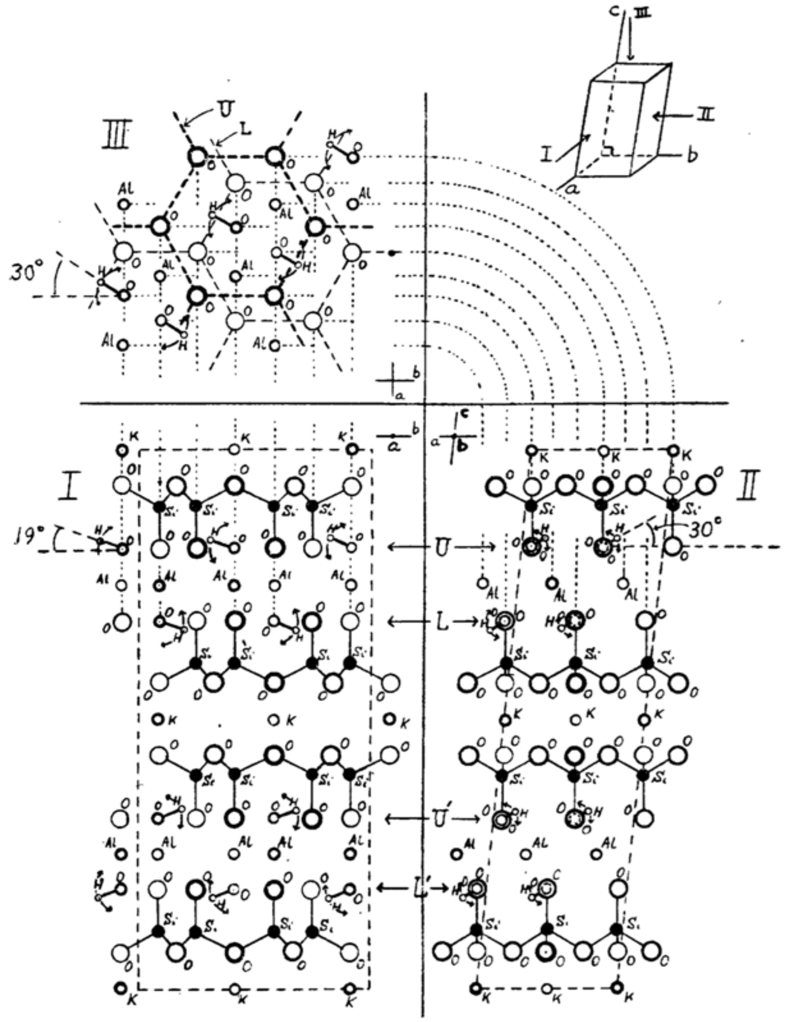

Fig. 6.—Crystal structure of muscovite. I: Projected on a plane normal to the *a* axis. II: Projected on 010. III: Projected on a cleavage plane.

Relative length ≒ 0.8.

(iii) The smallest axis: perpendicular to both of the greatest and the medium axes. Relative length is probably near to 0.

On the Position of the Hydrogen Atoms in Muscovite

The crystal structure of muscovite was studied by W. W. Jackson and J. West[4] by the X-ray method. According to them, each unit cell of muscovite includes eight OH groups distributed in four sheets, U, L, U′, and L′ in Figs. 5 and 6, parallel to 001, between the Al layer and the Si_2O_5 layer. The positions of the H atoms of these OH groups can be conjectured from the data of the infra-red absorption of muscovite described in this paper.

Table 4

O-H's on the U sheet...$\varphi=-129°$, $\psi=20°$
〃 〃 〃 L 〃 ...$\varphi=51°$, $\psi=-20°$
〃 〃 〃 U′ 〃 ...$\varphi=129°$, $\psi=20°$
〃 〃 〃 L′ 〃 ...$\varphi=-51°$, $\psi=-20°$

In Table 4 and Fig. 5 are shown the orientations of the O-H bonds on the assumption that the H atoms take fixed positions, their vibration being neglected. Here, by φ and ψ are denoted respectively the azimuth and the angle with 001 of each of the O-H bonds, in a similar way as those of the electric vector in Table 3. These values of φ, were determined so that $K_a/K_b = 0.63$, and ψ, so that the condition (ii) in the preceding section is satisfied. In Fig. 7 are given three principal sections of the theoretical *K-E* surface based on the calculations from the values of φ and ψ in Table 4. The points marked with ∘ represent the observed values of absorption coefficients. The coincidence of the theoretical and observed values of *K* is rather satisfactory.

It would seem inconceivable that φ's for the O-H bonds in muscovite take such values

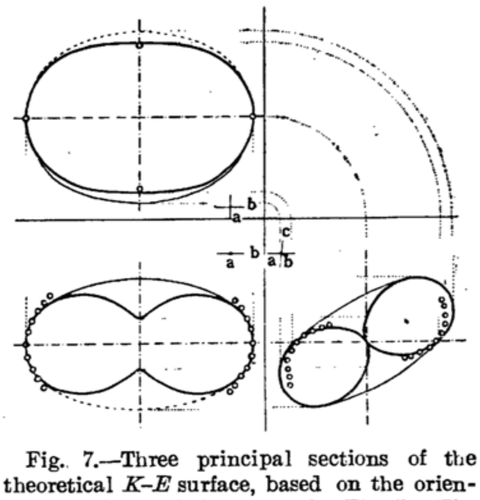

Fig. 7.—Three principal sections of the theoretical *K–E* surface, based on the orientations of the OH groups in Fig. 5. The points marked with ∘, represent the observed values of *K*.

as $-129°$, $51°$, $129°$ and $-51°$, in spite of the hexagonal arrangement of all the other neighbouring atoms. It would be more probable that the O-H bonds are orientated so that their azimuths (φ) are $-120°$, $60°$, $120°$ and $-60°$. But then, the value of K_a/K_b should be 0.33 instead of 0.63, the observed value. This deviation, however, can be explained as due to the vibration of the H atoms around their equilibrium positions.

Taking all of what have been said above into consideration, the probable orientations of the O-H bonds at equilibrium in muscovite are as shown in Table 5 and Fig. 6. The values in Table 4 are interpreted as representing

Table 5

O-H's on the U sheet	...$\varphi=-120°$,	$\phi=16.5°$
〃 〃 L 〃	...$\varphi=60°$,	$\phi=-16.5°$
〃 〃 U′ 〃	...$\varphi=120°$,	$\phi=16.5°$
〃 〃 L′ 〃	...$\varphi=-60°$,	$\phi=-16.5°$

the apparent orientations of the O-H bonds at 30°C. (at which the present experiment was carried on), resulted from the vibration of the H atoms around their equilibrium positions.

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