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Study on the Force Field of Quartz

By

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with 6 Tables and 1 Text-figure

ABSTRACT: The values for infrared absorption of quartz cut along the definite direction have been rescrutinized within the range of 1500∼400 cm^{-1} through transmission and reflection techniques, being well agreeable with the data and assignment proposed by SCOTT and PORTO. On the basis of their infrared and Raman spectra for α-quartz as well as the infrared data offered in the case of heating at 600°C by SIMON and McMAHON in association with the Raman data shown at 600°C by NARAYANASWAMY respectively for β-quartz the values of frequency for the fundamental vibration of quartz have been estimated in good harmony with those observed really in the experiments whereas it has become evident that the previous data for frequency were erroneously assigned to more or less extent. In view of the preceding works the data resulted from calculation of the wave-numbers of fundamental vibration for α- and β-quartz have been presented in this report.

CONTENTS

I. INTRODUCTION

Transformation from α- to β-quartz at ca. 570°C has so far been proved on the basis of convertibility in certain physical properties such as the coefficient of thermal expansion (Le CHATELIER, 1889), the specific heat (PERRIER and WOLFERS, 1920), the critical point appearing due to ascension of temperature and to variation of the Young modulus (PERRIER and MANDROT, 1923), the constant of piezo-electricity (PITT and McKINLEY, 1936) and so forth. In relation to these data, those combined with the force field of the inner structures have also been given by some authors. At the same time the constants for elasticity and compressibility have been evaluated from the force constants determined after the UREY-BRADLEY force field composed of four kinds of the force constants so as to make them agreeable with the observed values for frequency of vibration and specific heat from the calculated data for the latter (SAKSENA, 1940), while the elastic constant has been derivable more effectively from F^{-1} matrix or potential energy with respect to several terms such as those for the internal rotation, intramolecular tension, bond interaction, and trans-coupling in addition to the UREY-BRADLEY force field (SHIRO, 1968) and the data for the fundamental vibration in quartz have been presented by BARRIOL (1946) in the same manner as that pointed out by SAKSENA.

In the light of the researches enlightened previously the present work is aiming either at re-inspection of assignment of vibrations in the inner structure as well as correction of the data given for α-quartz by SHIRO (1968) as the first step for studying the lattice dynamics or at clarification of significance of the complementary terms in calculation of the fundamental frequencies of vibration as to β-quartz concerning the modified UREY-BRADLEY force field.

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II. STRUCTURES OF QUARTZ

It is well known that the structure of α-quartz is grouped into $D_3^4(P3_12)$ or $D_3^6(P3_22)$ and that of β-quartz into $D_6^4(C6_22)$ or $D_6^5(C6_42)$ and accordingly in the case of β-quartz the elements of symmetry: $2C_6^z$, $3C_2^y$ and C_2^z are to be added to those of α-quartz: $2C_3^z$ and $3C_2^x$.

Since 3 silicon atoms and 6 oxygen atoms are contained in the unit cells of α- and β-quartz, 16 species of optical vibration are expected from the factor group analysis, being separated as follows:

$$\Gamma = 4A + 4B + 8E \qquad \text{for } \alpha\text{-quartz}$$

and

$$\Gamma = 1A_1 + 3B_1 + 2A_2 + 2B_2 + 4E_1 + 4E_2 \qquad \text{for } \beta\text{-quartz}$$

where A and B species are non-degenerate and E degenerate, and according to the selection rule A, A_1 and E_2 species are Raman active, B and A_2 species infrared active, E and E_1 species Raman and infrared active, and B_1 and B_2 species inactive, as are revealed in Table 1. The relation of one to the other modification is shown in the following:

$$\begin{array}{lccc} \alpha\text{-quartz} & A(4) & B(4) & E(8) \\ & \swarrow \quad \searrow & \swarrow \quad \searrow & \swarrow \quad \searrow \\ \beta\text{-quartz} & A_1(1)\ B_1(3) & A_2(2)\ B_2(2) & E_1(4)\ E_2(4) \end{array}$$

On account of addition of $2C_6^z$, C_2^z and so on to the symmetry one of A species of α-quartz becomes symmetrical with $2C_6^z$ of β-quartz and thence belongs to A_1 species of the latter while the remaining three are antisymmetrical with $2C_6^z$ and correspond to B_1 species. Similarly B species of α-quartz are separated into A_2 and B_2 species owing to whether it may be symmetrical or antisymmetrical with $2C_6^z$

of β-quartz and E species of the former into E_2 and E_1 species of the latter because of whether it may be symmetrical or antisymmetrical with C_2^z.

The lattice constants determined accurately by JAY (1933) and the parameters of unit cell given by YOUNG *et al* (1962) have been provided as the parameters of the structures under consideration in the case of calculation of **B** and **A** matrix, when the data at 27°C have been used for α-quartz and those at 600°C for β-quartz.

TABLE 1. FACTOR GROUP ANALYSIS AND CHARACTERISTIC OF QUARTZ

GROUP D_3: α-QUARTZ

Species	E	$2C_3^z$	$3C_2^x$	N	T	n	Activity
A	1	1	1	4	0	4	Raman
B	1	1	−1	5	1	4	infrared
E	2	0	0	9	1	8	Raman and infrared

GROUP D_6: β-QUARTZ

Species	E	$2C_6^z$	$2C_3^z$	C_2^z	$3C_2^x$	$3C_2^y$	N	T	n	Activity
A_1	1	1	1	1	1	1	1	0	1	Raman
A_2	1	1	1	1	−1	−1	3	1	2	inrared
B_1	1	−1	1	−1	1	−1	3	0	3	
B_2	1	−1	1	−1	−1	1	2	0	2	
E_1	2	−1	−1	−2	0	0	5	1	4	Raman and infrared
E_2	2	1	−1	2	0	0	4	0	4	Raman

III. EXPERIMENTS AND THE OBSERVED DATA FOR FREQUENCY

As for optical vibration of α-quartz numerous data have hitherto been presented by many authors, a part of which are mentioned in Table 2. Inspection of the table clearly indicates miscellany of the values related to the infrared-active B species

TABLE 2. THE OBSERVED DATA FOR FREQUENCY (cm^{-1}) OF α-QUARTZ

Species	SAKSENA (1940)	KRISHNAN (1945)	BARRIOL (1946)	SIMON and McMAHON (1953)	LIPPINCOTT (1962)	SCOTT and PORTO (1967)	YAMAGUCHI
A	1082	1082	1082			1085	
	466	467	466			464	
	356	358	356			356	
	207	207	207			207	
B	1149		1190 (1227)	1055	1150	1080	1081
	777	805	800	790	780	778	775
	508	480	488		513	495	503
	364	378	385		374	364	

TABLE 2. (Continued)

Species	SAKSENA (1940)	KRISHNAN (1945)	BARRIOL (1946)	SIMON and McMAHON (1953)	LIPPINCOTT (1962)	SCOTT and PORTO (1967)	YAMAGUCHI
E	1159	1160	1248	1162	1176	1162	1163
	1063	1065	1163	1065	1097	1072	1075
	795∼807	794	798	795∼802	801	795	795 (802)
	695	696	696	695	695	696	694
	475				462∼475	450	475
	392∼403	404	394		397	394	
	265	266	267			265	
	128	128	127			128	

(1080 and 495cm^{-1}) and E species (1163, 1072 and 450cm^{-1}). In the present study, the sections of α-quartz cut along certain directions (e.g. X-, Y-, Z- and V-cut) have been subjected to infrared spectroscopy within the range of 1500∼400cm^{-1} by means of transmission and reflection methods. The spectroscope of *Shimazu* IR-27C *type* combined with the polarization apparatus and *KBr prism* has been provided for experiments. The results obtained for the X-cut sections parallel and normal to c axes with radiation of the polarized ray as well as those the Z-cut with radiation of the ordinary ray are illustrated in Fig. 1, wherein the obscure parts at 1250∼1000 cm^{-1}, 820∼740cm^{-1} and 530∼400cm^{-1} obtained through the transmission method are corrected by the results obtained through the reflection method in comparison with the data for polystyrene. As are shown in Table 1, the data for B species are recognized in polarized infrared absorption for the X-cut section parallel to c axis and those for E species in that for the similar section normal to c axis and for the Z-cut. Since the facts that for B species 1081, 775, 524 and 503cm^{-1} are discernible in the reflection data and 775cm^{-1} in the transmission data while for E species 1163, 1075, 802, 795 and 475cm^{-1} are so in the former case and 805, 798 and 694cm^{-1} in the latter are well accordant with those given by SCOTT and PORTO (1967), both values have been taken as the observed data for frequency.

As for β-quartz the Raman data found as the results of continuous heating by NARAYANASWAMY (1948) and the infrared absorption data obtained within the range of 1500∼700cm^{-1} with the similar treatment by SIMON and McMAHON (1953) have been applied to further calculation. It is to be taken into account that the reports made public by SAKSENA and NARAIN (1949) and SCOTT and PORTO (1967) as to assigment of these data are considerably erroneous.

Historically, SAKSENA and NARAIN (1949) gave assignment of the Raman data obtained for β-quartz by NARAYANASWAMY on the basis of the vibration mode of α-quartz: that is, 1154cm^{-1} of β-quartz is in an intimate relation to 1163cm^{-1} of the infrared- and Raman-active E species in the case of α-quartz and to E_1 species under consideration of the vibration mode and 1060cm^{-1} of β-quartz to E_2 species.

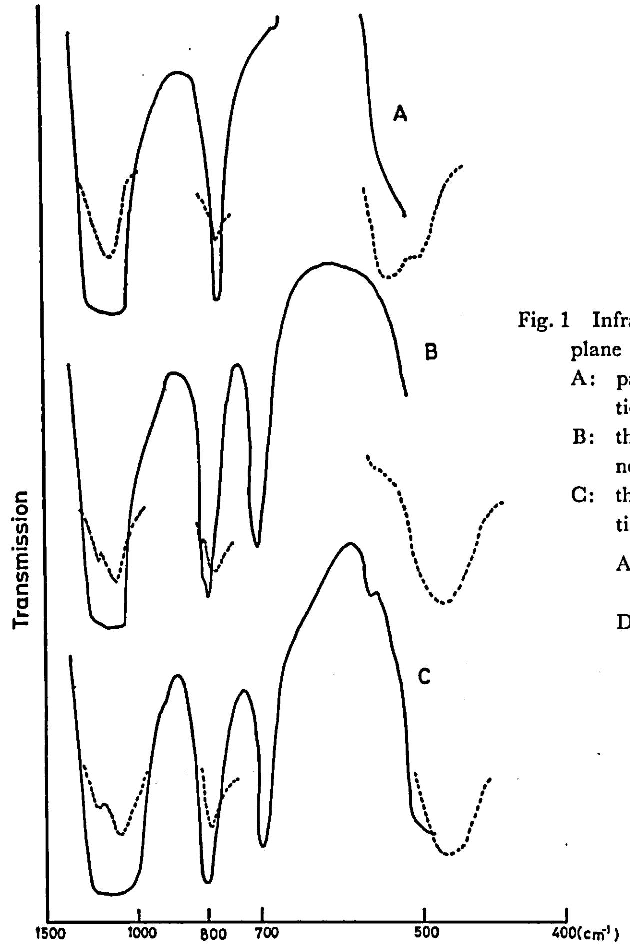

Fig. 1 Infrared absorption spectra on each oriented plane
A: pattern for *X*-cut with polarized radiation parallel to *c* axis
B: that for *X*-cut with polarized radiation normal to *c* axis
C: that for *Z*-cut with non-polarized radiation

Actual lines: those obtained through transmission method
Dotted lines: those obtained through reflection method but drawn from the overturned figures

That with continuous heating of α- to β-quartz the infrared absorption of the former at $1163\,\mathrm{cm}^{-1}$ is gradually convertible to that at $1154\,\mathrm{cm}^{-1}$ and disappear near the transition temperature was reported by SIMON and McMAHON, pointing to misplaying by SAKSENA and NARAIN in assignment of $1154\,\mathrm{cm}^{-1}$ for E_1 species. The data for factor group analysis are considered to bring out mistake in the opinion given by SIMON and McMAHON that $1154\,\mathrm{cm}^{-1}$ is concerned with E species in the case of α-quartz and however with some of A species in the case of β-quartz. In more detail it is to be noted that the absorption in question is correlative to that at $1163\,\mathrm{cm}^{-1}$ of E species for α-quartz and to the infrared-inactive and Raman-active E_2 species for β-quartz and accordingly that at $1060\,\mathrm{cm}^{-1}$ connected with E_2 species by SAKSENA and NARAIN is to be assigned to E_1 species, as are deducible from the infrared data of SIMON and McMAHON.

For β-quartz 97 and $250\,\mathrm{cm}^{-1}$ are combined respectively with E_1 and E_2 species by SAKSENA and NARAIN while the reverse assignment is theoretically derived from the wave theory suggested by SCOTT and PORTO. Moreover it is known from the data of α-quartz given by SHIRO (1968) that $265\,\mathrm{cm}^{-1}$ implies nearly antisymmetry and $128\,\mathrm{cm}^{-1}$ almost symmetry respectively for $C_2{}^z$. Calculation of frequency in the present investigation has been based on his assingment.

IV. CALCULATION OF FREQUENCY

The wave-numbers for the fundamental vibration of quartz have been evaluated concerning the Cartesian symmetry coordinate X_{SM} treated with mass regulation. Then the equations of kinetic energy T and potential energy V are written as:

$$T=\frac{1}{2}\tilde{\dot{X}}_{SM}\dot{X}_{SM}$$

$$V=\frac{1}{2}\tilde{X}F_{XSM}X_{SM}$$

where F_{XSM} is the potential energy matrix referred to Cartesian symmetry coordinate and expressed referring to the internal symmetry coordinate as:

$$\begin{aligned}F_{XSM}&=M^{-\frac{1}{2}}U_X\tilde{B}FB\tilde{U}_XM^{-\frac{1}{2}}\\&=U_{XM}\tilde{B}FB\tilde{U}_{XM}\end{aligned}$$

where U_X is the Cartesian symmetry matrix, M the mass matrix and B the transformation matrix between the rectangular and internal coordinates.

Accordingly the secular equation is:

$$|F_{XSM}-E\lambda|=0$$

From the eigen value λ in the equation the frequency $\bar{\nu}$ is derivable from:

$$\begin{aligned}\bar{\nu}&=\frac{\sqrt{N\times10^5}}{2\pi C}\times\sqrt{\lambda}\qquad(N:\ \text{Avogadro number})\\&=1303.15804\sqrt{\lambda}\end{aligned}$$

The vaues for each element J_{ih} of Jacobian matrix (representing the effects accompanied with variation of 1 m dyne/Å for each force constant) are expressed as:

$$J_{ih}=(\tilde{L}_{XSM}A_{XSMh}L_{XSM})_{ii}$$

Ratio of the potential energy distribution for each force constant in each mode of vibration is:

$$(P.E.D.)_{ih}=\frac{J_{ih}K_h}{\lambda_i}$$

It is here to be remarked that the correct values for potential energy are of course derived from determination of the correct values for the force constants.

V. RESULT AND DISCUSSION

The assumed form of the modified UREY-BRADLEY force field is:

$$2V=\sum_i K(\text{Si-0})(\Delta r_i)^2+\sum_i H_1(\text{0-Si-0})r^2(\Delta\alpha_i)^2+\sum_i F_1(\text{0-Si-0})\Delta q_i^2(0\cdots 0)$$
$$+\sum_i H_2(\text{Si-0-Si})r^2(\Delta\beta_i)^2+\sum_i F_2(\text{Si-0-Si})\Delta q_i^2(\text{Si}\cdots\text{Si})+Y(\Delta\tau_i)^2$$
$$+2\sum_{i,j}\kappa(\Delta\alpha_i)(\Delta\alpha_j)+2\sum_{i,j}P(\Delta r_i)(\Delta r_j)$$

where $K(\text{Si—0})$ is the force constant of stretching, $H_1(\text{0—Si—0})$ and $H_2(\text{Si—0—Si})$ those of bending, $F_1(0\cdots 0)$ and $F_2(\text{Si}\cdots\text{Si})$ those of repulsion, Y that of the internal

TABLE 3. THE OBSERVED AND CALCULATED DATA FOR FREQUENCY (cm^{-1}) OF QUARTZ

α-QUARTZ β-QUARTZ

Spec.	Obs.* Freq.	Calc. Freq.		Mode	Spec.	Obs.** Freq.	Calc. Freq.		Mode
		Set I	Set II				Set I	Set II	
A	1085	1087	1081	Si-0 str.	A_1	453	424	437	skel. def.
	464	468	485	skel. def.	B_1		1130	1080	Si-0 str.
	356	356	366	skel. def.			390	402	skel. def.
	207	178	194	torsional			78	81	torsional
B	1081	1092	1081	Si-0 str.	A_2	(1072)	1102	1060	Si-0 str.
	778	777	776	skel. def.		(490)	534	535	skel. def.
	503	575	587	skel. def.	B_2		760	746	skel. def.
	364	391	398	skel. def.			446	463	skel. def.
E	1163	1090	1135	Si-0 str.	E_1	1060	1104	1070	Si-0 str.
	1075	1058	1084	Si-0 str.		785	788	773	skel. def.
	795	785	783	skel. def.		(470)	507	505	skel. def.
	694	691	706	skel. def.		97	135	137	torsional
	475	517	521	skel. def.	E_2	1154	1080	1130	Si-0 str.
	394	359	362	skel. def.		686	662	669	skel. def.
	265	250	251	skel. def.		395	361	366	skel. def.
	128	127	138	torsional		250	250	250	skel. def.

* YAMAGUCHI, H. …infrared spectra
SCOTT, J.F. and PORTO, S.P.S. (1967) …Raman spectra
** SIMON, I. and McMAHON, H.O. (1953) …infrared spectra at 600°C
NARAYANASWAMY, P.K. (1948) …Raman spectra at 600°C
( ): estimated value from the frequency of α-quartz

rotation, κ that of the intramolecular tension and P that of the bond-interaction respectively.

The force field has been determined through the least square method with use of the Jacobian matrix. The calculated data for frequency and the force constants are alined in Tables 3 and 4. The values obtainedfor the wave-numbers of α- and β-quartz point to such a slight difference as $10\sim30\,\mathrm{cm}^{-1}$ and in consequence almost no difference among their force constants.

TABLE 4. THE FORCE CONSTANTS OF QUARTZ

	α-QUARTZ		β-QUARTS		Dimension
	Set I	Set II	Set I	Set II	
K(Si-0)	3. 981	4. 213	3. 983	4. 023	md/Å
H_1(0-Si-0)	0. 043	0. 048	0. 048	0. 048	〃
F_1(0···0)	0. 398	0. 400	0. 400	0. 400	〃
H_2(Si-0-Si)	0. 019	0. 009	0. 009	0. 009	〃
F_2(Si···Si)	0. 664	0. 664	0. 664	0. 664	〃
Y	0. 000	0. 005	0. 005	0. 005	md•Å
κ	0. 550	0. 550	0. 550	0. 550	〃
P	0. 000	0. 280	0. 000	0. 302	md/Å

K: stretching, H: bending, F: repulsion, Y: internal rotation, κ: intramolecular tension, P: bond-interaction

TABLE 5. JACOBIAN MATRICES OF QUARTZ

α-QUARTZ

Species	Calc. Freq.	K	H_1	F_1	H_2	F_2	Y	κ	P
A	1081	0. 160	0. 040	0. 135	0. 004	−0. 002	0. 007	0. 007	−0. 160
	486	0. 010	0. 212	0. 123	0. 227	0. 025	0. 012	0. 019	0. 030
	366	0. 001	0. 263	0. 106	0. 005	0. 001	0. 216	0. 028	0. 004
	194	0. 001	0. 099	0. 043	0. 006	0. 001	0. 384	−0. 012	0. 002
B	1086	0. 161	0. 075	0. 093	0. 038	0. 004	0. 057	0. 031	−0. 160
	776	0. 056	0. 183	0. 038	0. 003	0. 111	0. 202	0. 075	−0. 056
	578	0. 001	0. 347	0. 155	0. 331	0. 052	0. 023	0. 142	−0. 001
	398	0. 003	0. 159	0. 089	0. 012	0. 003	0. 427	0. 065	−0. 003
E	1135	0. 129	0. 033	0. 342	0. 003	0. 005	0. 007	0. 009	0. 177
	1084	0. 159	0. 095	0. 097	0. 027	0. 002	0. 050	0. 037	−0. 158
	783	0. 050	0. 386	0. 049	0. 145	0. 063	0. 078	0. 104	−0. 056
	706	0. 043	0. 160	0. 063	0. 050	0. 065	0. 055	0. 064	−0. 002
	521	0. 001	0. 325	0. 138	0. 103	0. 022	0. 351	0. 124	−0. 001
	362	0. 002	0. 242	0. 109	0. 115	0. 022	0. 131	−0. 002	−0. 000
	251	0. 000	0. 113	0. 049	0. 114	0. 018	0. 140	−0. 006	−0. 000
	139	0. 000	0. 037	0. 015	0. 020	0. 004	0. 341	−0. 003	−0. 000

TABLE 5. (Continued) β-QUARTZ

A_1	437	0.007	0.358	0.173	0.236	0.025	0.000	−0.050	0.021
B_1	1080	0.169	0.017	0.137	0.000	−0.002	0.024	0.007	−0.169
	402	0.000	0.212	0.083	0.000	−0.000	0.463	0.089	−0.000
	81	0.000	0.000	0.000	0.000	−0.000	0.754	0.000	−0.000
A_2	1060	0.165	0.068	0.100	0.000	−0.002	0.229	0.029	−0.165
	535	0.000	0.367	0.150	0.000	−0.000	1.235	0.154	−0.000
B_2	746	0.046	0.186	0.019	0.112	0.145	0.001	0.078	−0.046
	463	0.006	0.155	0.103	0.244	0.026	0.009	0.065	−0.006
E_1	1070	0.164	0.086	0.096	0.034	0.003	0.078	0.036	−0.164
	773	0.054	0.293	0.046	0.119	0.072	0.002	0.123	−0.054
	505	0.002	0.271	0.116	0.111	0.028	0.427	0.114	−0.002
	137	0.000	0.007	0.003	0.042	0.007	0.489	0.003	−0.000
E_2	1130	0.133	0.034	0.362	0.000	0.005	0.017	0.006	0.191
	669	0.037	0.184	0.059	0.004	0.063	0.249	0.072	−0.001
	366	0.002	0.258	0.117	0.104	0.011	0.568	−0.001	−0.000
	250	0.000	0.166	0.068	0.132	0.018	0.189	−0.023	−0.000
Unit	cm^{-1}	Å/md·sec^2	〃	〃	〃	〃	1/Å·md·sec^2	〃	Å/md·sec^2

The Jacobian matrix for the force constants and the distribution of potential energy are disposed in Tables 5 and 6.

In the case of β-quartz B_1 and B_2 species are Raman and infrared inactive, whereas it may be that the corresponding frequencies are present but not recognizable due to the property of symmetry.

That some deviation and decrement of the wave-number corresponding to 207 cm^{-1} become more conspicuous with transformation from α- to β-quartz has been alluded to already by NARAYANASWAMY. On the other hand that no data related to 207 cm^{-1} for β-quartz (corresponding to that for α-quartz) have, as if essentially none in

TABLE 6-1. RATIO OF THE POTENTIAL ENERGY DISTRIBUTION FOR EACH FORCE CONSTANT OF SET I.

α-QUARTZ

Species	Obs. Freq. (cm^{-1})	Calc. Freq. (cm^{-1})	K	H_1	F_1	H_2	F_2	Y	κ
A	207	178	0.204	0.218	0.876	0.006	0.034	0.019	−0.338
E	1163	1090	0.943	0.006	0.058	0.001	0.002	00.00	0.030
	1075	1058	0.779	0.002	0.203	0.000	0.005	0.000	0.008
	265	250	0.000	0.137	0.552	0.061	0.338	0.004	−0.093
	128	127	0.000	0.171	0.642	0.031	0.296	0.037	−0.178

TABLE 6-1. (Continued) β-QUARTZ

Species	Obs. Freq. (cm^{-1})	Calc. Freq. (cm^{-1})	K	H_1	F_1	H_2	F_2	Y	κ
B_1		78	0.000	0.000	0.000	0.000	−0.000	0.987	0.000
E_1	1060	1104	0.909	0.006	0.053	0.001	0.003	0.001	0.028
	97	135	0.000	0.032	0.112	0.029	0.442	0.049	0.155
E_2	1154	1080	0.776	0.002	0.212	0.000	0.005	0.000	0.005
	250	250	0.000	0.218	0.743	0.032	0.327	0.026	−0.346

evaluation of the values for frequency, been obtained by BARRIOL (1946) and SAKSENA and NARAIN is therefore probably resulted from calculation only on the basis of UREY-BRADLY force field regardless of the internal rotation and in other words ascribable to the mere effect of the potential energy concerned with the internal rotation in the case of β-quartz (Table 6–2).

As for assignment of the observed data for frequency in the case of β-quartz, it is worthy mentioning that 97 cm^{-1} is combined with E_1 species and 250 cm^{-1} with E_2 species by SAKSENA and NARAIN while on the contrary the former is connected with E_2 and the latter with E_1 by SCOTT and PORTO. In the case of their assignment, however, the distribution of potential energy clearly suggests that 265cm^{-1} in E species of α-quartz is correlative to 97 cm^{-1} in E_2 species of β-quartz and 128 cm^{-1} in E species of the former to 250 cm^{-1} in E_1 species of the latter. Since this is in opposition to NARAYANASWAMY's assignment that 265 cm^{-1} of α-quartz is annexed to 250 cm^{-1} of β-quartz and 128 cm^{-1} to 97 cm^{-1}, the opinion given by SAKSENA and NARAIN that 97 cm^{-1} pertains to E_1 species and 250 cm^{-1} to E_2 species is naturally justifiable. On the other hand the force constants of quartz are grouped into two sets, of which the first is related to K, H_1, F_1, H_2, F_2, Y and κ and the second contains the bond interaction P in addition to all of the former, as are arranged in Table 4. Taking account of the set I without any consideration of P, it seems reasonable that in the case of β-quartz 1104 cm^{-1} obtained from calculation corresponds to the observed value 1060 cm^{-1} in E_1 species and 1080 cm^{-1} to 1154 cm^{-1} in E_2 species while in the case of α-quartz the calculated value 1090 cm^{-1} is closely related to 1163 cm^{-1} in E species and 1058 cm^{-1} to 1075 cm^{-1} in the same species, although, as are obvious in Table 6, it is also proven from inspection of the potential energy distribution that the calculated 1090 cm^{-1} is concerned with the observed 1075 cm^{-1} and 1058 cm^{-1} with 1163 cm^{-1}. This surely points to that in the case of assignment proposed by SAKSENA (1940), BARRIOL (1946), SAKSENA and NARAIN (1949) and SHIRO (1968) on the basis of force field of the lattice concerned the opposite relations were offered for 1075 cm^{-1} (1060 cm^{-1}) and 1163 cm^{-1} (1154 cm^{-1}). It thus results in that the data for the force field arranged in the set II are more reliable concerning both modifications of quartz and the bond interaction is a remarkably significant factor for considering the potenial energy.

TABLE 6-2. RATIO OF THE POTENTIAL ENERGY DISTRIBUTION FOR EACH FORCE CONSTANT OF SET II.

α-QUARTZ

Species	*A*				*B*				*E*							
Obs. Freq. (cm^{-1})	464	1085	356	***207***	1081	503	778	364	***1075***	795	475	***128***	***1163***	694	394	***265***
Calc. Freq. (cm^{-1})	485	1081	366	***194***	1086	578	776	398	***1084***	783	521	***138***	***1135***	706	362	***251***
K	0.304	0.979	0.054	***0.208***	0.967	0.021	0.667	0.092	***0.973***	0.677	0.027	***0.000***	***0.736***	0.603	0.110	***0.000***
H_1	0.073	0.003	0.159	***0.244***	0.005	0.084	0.025	0.084	***0.007***	0.038	0.098	***0.157***	***0.038***	0.026	0.151	***0.146***
F_1	0.355	0.078	0.539	***0.869***	0.054	0.314	0.032	0.389	***0.056***	0.054	0.346	***0.529***	***0.054***	0.086	0.569	***0.526***
H_2	0.015	0.002	0.001	***0.003***	0.000	0.015	0.000	0.001	***0.000***	0.004	0.006	***0.016***	***0.000***	0.002	0.014	***0.028***
F_2	0.012	0.000	0.000	***0.003***	0.004	0.175	0.208	0.021	***0.000***	0.116	0.092	***0.235***	***0.005***	0.147	0.191	***0.321***
Y	0.000	0.000	0.014	***0.086***	0.000	0.001	0.003	0.023	***0.002***	0.001	0.011	***0.151***	***0.000***	0.001	0.008	***0.018***
κ	0.071	0.006	0.212	***−0.533***	0.025	0.396	0.115	0.397	***0.029***	0.160	0.434	***−0.146***	***0.007***	0.118	−0.014	***0.086***
P	0.061	−0.065	0.014	***0.028***	0.065	−0.001	−0.044	−0.006	***−0.064***	−0.043	−0.002	***0.000***	***0.067***	0.003	−0.000	***−0.000***

β-QUARTZ

Species	*A₁*	*B₁*			*A₂*		*B₂*		*E₁*				*E₂*			
Obs. Freq. (cm^{-1})	453				(1072)	(487)			***1060***	785	(470)	***97***	***1154***	686	395	***250***
Calc. Freq. (cm^{-1})	437	1080	402	***81***	1060	535	746	463	***1070***	773	505	***137***	***1130***	669	366	***250***
K	0.251	0.989	0.000	***0.000***	0.989	0.000	0.564	0.191	***0.974***	0.617	0.053	***0.000***	***0.717***	0.564	0.103	***0.000***
H_1	0.153	0.001	0.107	***0.000***	0.005	0.104	0.027	0.059	***0.061***	0.041	0.086	***0.032***	***0.002***	0.033	0.158	***0.216***
F_1	0.617	0.080	0.349	***0.000***	0.059	0.355	0.023	0.326	***0.057***	0.052	0.308	***0.118***	***0.194***	0.089	0.597	***0.737***
H_2	0.019	0.000	0.000	***0.000***	0.000	0.000	0.003	0.017	***0.000***	0.005	0.007	***0.035***	***0.000***	0.000	0.012	***0.032***
F_2	0.148	−0.002	0.000	***−0.000***	−0.002	−0.000	0.294	0.137	***0.003***	0.136	0.124	***0.436***	***0.004***	0.159	0.093	***0.324***
Y	0.000	0.000	0.024	***0.975***	0.002	0.037	0.000	0.000	***0.000***	0.000	0.014	***0.229***	***0.000***	0.005	0.036	***0.026***
κ	−0.245	0.006	0.515	***0.000***	0.024	0.502	0.131	0.283	***0.029***	0.123	0.379	***0.154***	***0.004***	0.150	−0.007	***−0.350***
P	0.057	−0.074	0.000	***−0.000***	−0.074	−0.000	−0.042	−0.014	***−0.073***	−0.046	−0.004	***−0.000***	***0.077***	−0.001	−0.000	***−0.000***

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