

## Study of the Force Field and the Vibrational Normal Modes in the $\alpha$ - $\beta$ Quartz Phase Transition

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### Abstract

A theoretical study of the force field and the vibrational modes of  $\alpha$  and  $\beta$  quartz between room temperature and 600°C has been carried out at various temperatures, using some recent experimental results. It is shown that a modified Urey-Bradley force field can account for the optical frequencies of  $\alpha$  and  $\beta$  quartz. The value of the internal rotation force constant is negative during the  $\alpha$ - $\beta$  phase transition, and zero in the case of  $\beta$  quartz. The vibrational mode of the 207  $\text{cm}^{-1}$   $A_1$  mode, known to be a soft mode, becomes more in agreement with displacements involved in the  $\alpha$ - $\beta$  phase transition as the transition temperature  $T$  is approached from below.

The infrared intensities were also calculated from atomic displacements, using the two-charge model of Kleinman and Spitzer. The results confirm the calculated normal modes.

### Introduction

The number of available infrared and Raman spectra connected with the vibrational modes of the two crystallographic polymorphs of quartz is very large. A review of optical lattice vibrations in quartz was published by Scott and Porto (1967). Several assignments of the  $E_1$  and  $E_2$  modes in  $\beta$  quartz by them, however, differed from the assignments proposed earlier by Saksena and Narain (1949). Reliable assignments for these modes were proposed by Yamaguchi, Iishi, and Umegaki (1971) on the basis of theoretical calculations of frequencies of  $\alpha$  and  $\beta$  quartz. Their assignments have been proved correct by Bates and Quist (1972) using polarized Raman spectra of  $\beta$  quartz. Yamaguchi *et al*'s assignments will thus be accepted in the present work.

Quartz undergoes a transition at 573°C from the low-temperature  $\alpha$  phase with symmetry  $D_3$  to the high-temperature  $\beta$  phase with symmetry  $D_6$ . This transition has been studied by several investigators in terms of lattice dynamics. The analysis of Kleinman and Spitzer (1962) and of Elcombe (1967) are similar, and each elaborates on the basic conclusion of Saksena's (1940 and 1949) early force constant calculation: that the frequency of the 207  $\text{cm}^{-1}$  mode should approach zero as the transition temperature  $T$

is approached from below. Kleinman and Spitzer (1962) found that the atomic displacements at the transition correspond closely to the 207  $\text{cm}^{-1}$  mode.

Narayanaswamy (1948) observed the temperature-dependent Raman spectrum of quartz and found that the 207  $\text{cm}^{-1}$  line does indeed show strong variation with temperature, moving toward the Rayleigh line as the transition temperature is approached, and disappearing completely in the  $\beta$  phase. From a study of the Raman spectra of quartz at temperatures between -196 and 615°C, however, Shapiro, O'Shea, and Cummins (1967) proposed that the 147  $\text{cm}^{-1}$  mode, rather than the 207  $\text{cm}^{-1}$  mode, appeared to play a fundamental role in the phase transition. From work on the Raman spectrum of quartz at 6°K to 900°K, Scott (1968) and Höchli and Scott (1971) presented evidence that the frequency of the 207  $\text{cm}^{-1}$  mode approaches zero as the transition temperature is approached from below. On the basis of the relative atomic displacements of the 207  $\text{cm}^{-1}$  mode associated with critical neutron scattering, Axe and Shirane (1970) obtained a remarkable similarity between this mode and the displacements involved in the  $\alpha$ - $\beta$  phase transition. Thus they have concluded that the room temperature renormalized soft mode is not at 147  $\text{cm}^{-1}$  as proposed by Shapiro *et al* (1967) but is rather at 207  $\text{cm}^{-1}$ . It has, therefore, been

TABLE 1. Decomposition of the Normal Mode of Quartz into Symmetry Species

Crystal	Spatial symmetry	Optic vibration
$\alpha$ quartz	$D_3^h$	$4A_1+4A_2+8E$
$\beta$ quartz	$D_6^h$	$A_1+3B_1+2A_2+2B_2+4E_1+4E_2$

generally accepted that the  $207\text{ cm}^{-1}$  mode is in fact the lattice vibration fundamentally associated with the  $\alpha$ - $\beta$  phase transition, *i.e.*,  $207\text{ cm}^{-1}$  mode in quartz is a soft mode.

This paper examines the effects of force constants and change of vibrational mode and frequencies of the soft  $A_1$   $207\text{ cm}^{-1}$  mode during the  $\alpha$ - $\beta$  phase transition through a theoretical calculation of the lattice dynamics of quartz. To check the correctness of the determined normal modes, the infrared intensities were also calculated.

### Selection Rules and Coordinates

The primitive cells of the  $\alpha$  and  $\beta$  polymorphs of  $\text{SiO}_2$  contain three silicon atoms and six oxygen atoms. The symmetry species of the  $D_3$  factor group

TABLE 2. Experimental Frequencies Used for the Calculation of the Urey-Bradley Force Field (Frequencies in  $\text{cm}^{-1}$ )

Symmetry	$\alpha$ quartz			$\beta$ quartz	
	25°C*	532°C**	552°C***	Symmetry	700°C**
$A_1$	1085	(1072) <sup>†</sup>		$B_1$	inactive
	464	460		$A_1$	464
	356	(350) <sup>†</sup>		$B_1$	inactive
	207	80 <sup>††</sup>	70 <sup>††</sup>	$B_1$	inactive
$A_2$	1080		1064	$A_2$	1061***
	778		777	$B_2$	inactive
	495		457	$A_2$	435***
	364	358	385	$B_2$	inactive
$E$	1162	1167	1155	$E_2$	1173
	1072	1066	1060	$E_1$	1065
	795	798	782	$E_1$	786
	697	690	680	$E_2$	686
	450	440	430	$E_1$	427
	394	397	400	$E_2$	407
	265	256		$E_2$	243
	128	110		$E_1$	98

\* Scott and Porto(1967)

\*\* Bates and Quist(1972)

\*\*\* Gervais(1974)

<sup>†</sup> Narayanaswamy, measured at 550°C

<sup>††</sup> These values were estimated from Fig. 1. of Höchli and Scott(1971).

The value of soft mode  $A_1$  was estimated about  $50\text{ cm}^{-1}$  at  $570^\circ\text{C}$ .

TABLE 3. Force Constants\* of Quartz at Various Temperatures

	$\alpha$ quartz			$\beta$ quartz
	25°C	520°C	570°C	600°C
$K$ (Si-O)	4.584	4.504	4.504	4.504
$H_1$ (O-Si-O)	0.154	0.154	0.154	0.154
$F_1$ (0***0)	0.196	0.196	0.196	0.196
$H_2$ (Si-O-Si)	0.000	0.000	0.000	0.000
$F_2$ (Si***Si)	0.485	0.485	0.485	0.485
$Y$	-0.004	-0.004	-0.004	0.000
$\kappa$	0.268	0.268	0.268	0.268
$p$	0.417	0.497	0.497	0.497

\*Units: stretching  $K$ , bending  $H$ , repulsion  $F$  and bond interaction  $p$  mdyne/Å; intramolecular tension  $\kappa$  and internal rotation  $Y$  mdyne\*Å.

of  $\alpha$  quartz and the symmetry species of the  $D_6$  factor group of  $\beta$  quartz are given in Table 1.

The 48 internal coordinates used in this work include 12 Si-O stretching coordinates ( $\Delta R$ ), 18 O-Si-O bending coordinates ( $\Delta\alpha$ ), 6 Si-O-Si bending coordinates ( $\Delta\beta$ ), and 12 Si-O internal rotation coordinates ( $\Delta Y$ ). The number of coordinates in each set was constrained by symmetry considerations. As shown by Shiro (1968), Yamaguchi *et al* (1971), and Etchepare, Merian, and Smetankine (1974), one must consider internal rotation coordinates in order to obtain an agreement with the vibrational spectra of  $\alpha$  and  $\beta$  quartz.

The coordinate parameters of  $\alpha$  quartz at room temperature have been accurately determined by Smith and Alexander (1963). The coordinate parameters of  $\alpha$  and  $\beta$  quartz have been accurately determined as a function of temperature at temperature from  $450^\circ\text{C}$  to  $650^\circ\text{C}$  by Young (1962). These data have been used in the potential energy and the kinetic energy matrices.

### Force Field and Vibrational Frequencies

The temperature dependences of the  $A_2$  and  $E$  vibration modes in quartz were measured over the temperature range from room temperature to a few degrees above the  $\alpha$ - $\beta$  phase transition temperature by Gervais (to be published). The Raman spectrum of a single crystal of quartz was measured over the temperature range from a few degrees below the  $\alpha$ - $\beta$  phase transition temperature to  $700^\circ\text{C}$  by Bates and Quist (1972). The experimental frequencies on which our calculations are based are listed in Table 2.

In order to determine a suitable force field for  $\alpha$  and  $\beta$  quartz, the normal frequencies were calculated by use of a modified Urey-Bradley force field. The general method for the treatment of the normal

TABLE 4. Observed and Calculated Frequencies of Quartz at Various Temperatures  
(Frequencies in  $\text{cm}^{-1}$ )

Symmetry	$\alpha$ quartz					$\beta$ quartz				
	25°C		520°C		570°C	Symmetry	Exptl.	600°C		
	Exptl.	Calc.	Calc.	Calc.	Calc.			Calc.	Calc.	Calc.
$A_1$	1085	1092	1083	(1104)	1088	(1109)	$B_1$	inactive	1096	(1116)
	464	482	465	(463)	465	(463)	$A_1$	461	468	(466)
	356	355	348	(355)	348	(356)	$B_1$	inactive	352	(356)
	207	208	130	(154)	87	(126)	$B_1$	inactive	12	(73)
$A_2$	1080	1100	1087	(1108)	1088	(1109)	$A_2$	1061	1088	(1109)
	778	760	737	(748)	731	(741)	$B_2$	inactive	724	(733)
	495	505	493	(496)	484	(490)	$A_2$	435	465	(474)
	364	353	361	(373)	374	(384)	$B_2$	inactive	407	(408)
$E$	1162	1122	1141	(1137)	1143	(1139)	$E_2$	1173	1145	(1173)
	1072	1098	1089	(1110)	1091	(1111)	$E_1$	1065	1092	(1113)
	795	775	754	(764)	756	(767)	$E_1$	786	760	(770)
	697	695	669	(674)	665	(671)	$E_2$	686	656	(661)
	450	464	449	(457)	444	(451)	$E_1$	427	443	(446)
	394	362	361	(367)	361	(370)	$E_2$	407	369	(376)
	265	247	246	(251)	251	(255)	$E_2$	243	260	(261)
	128	136	103	(128)	95	(123)	$E_1$	98	103	(118)

The values in parenthesis are obtained by presuming the same force constant values with those of  $\alpha$  quartz.

vibrations of crystals was reported by Shimanouchi, Tsuboi, and Miyazawa (1961). The supplementary terms of the force field are the internal rotation potential  $Y$  and the bond interaction potential for the pairs of the adjacent Si-O bonds  $p$ . We assume in the potential energy matrix that (1) the same stretching force constants and interactions pertain for the various Si-O lengths, and that (2) the same bending force constants pertain for all the O-Si-O and Si-O-Si angles.

Table 3 gives the values of force constants determined by the least squares method; it appears that 7 parameters are enough to fit the 24 experimental frequencies. Table 4 gives the calculated frequencies for  $\alpha$  quartz at 25, 520, and 570°C and  $\beta$  quartz at 600°C. The fit between experimental frequencies and calculated values is satisfactory. Etchepare *et al* (1974) obtained similar results for  $\alpha$  and  $\beta$  quartz on the basis of the general valence force field. But the physical meaning of their negative values of force constants and interaction terms is unclear. The repulsive force constants resulting from ionic bonding character in crystals seem to be necessary for crystals such as quartz in which the bonds have some ionic character. A simple valence force field which contains no terms responsible for ionic character seems to be unsuitable as a force field for quartz.

To examine the influence of potential energy associated with softness of the soft mode, the frequencies calculated under the assumption of the same force field for  $\alpha$  and  $\beta$  quartz are also listed in Table 4. Jacobian values of the 207  $\text{cm}^{-1}$  soft mode obtained for  $\alpha$  quartz at 25, 520, and 570°C and  $\beta$  quartz at 600°C are listed in Table 5. It is noteworthy that the Jacobian values of the 207  $\text{cm}^{-1}$  mode related to the internal rotation potential increase with increasing temperature, in contrast to the decreasing of those frequencies related to the bending potential and repulsion potential.

As reported by Scott (1968), Höchli and Scott (1971), and Bates and Quist (1972), the frequency of

TABLE 5. Jacobian Matrix of Soft Mode 207  $\text{cm}^{-1}$  in Quartz at Various Temperatures

	$\alpha$ quartz			$\beta$ quartz
	25°C	520°C	570°C	600°C
$K$	0.001393	0.000768	0.000450	0.000011
$H_1$	0.065377	0.031270	0.017909	0.000017
$F_1$	0.031738	0.015617	0.009024	0.000028
$H_2$	0.010547	0.012354	0.008603	0.000372
$F_2$	0.001610	0.001447	0.000977	0.000039
$Y$	0.292448	0.549317	0.658748	0.782839
$\kappa$	-0.002972	-0.003879	-0.002455	0.000020
$P$	0.004177	0.002292	0.001349	0.000000

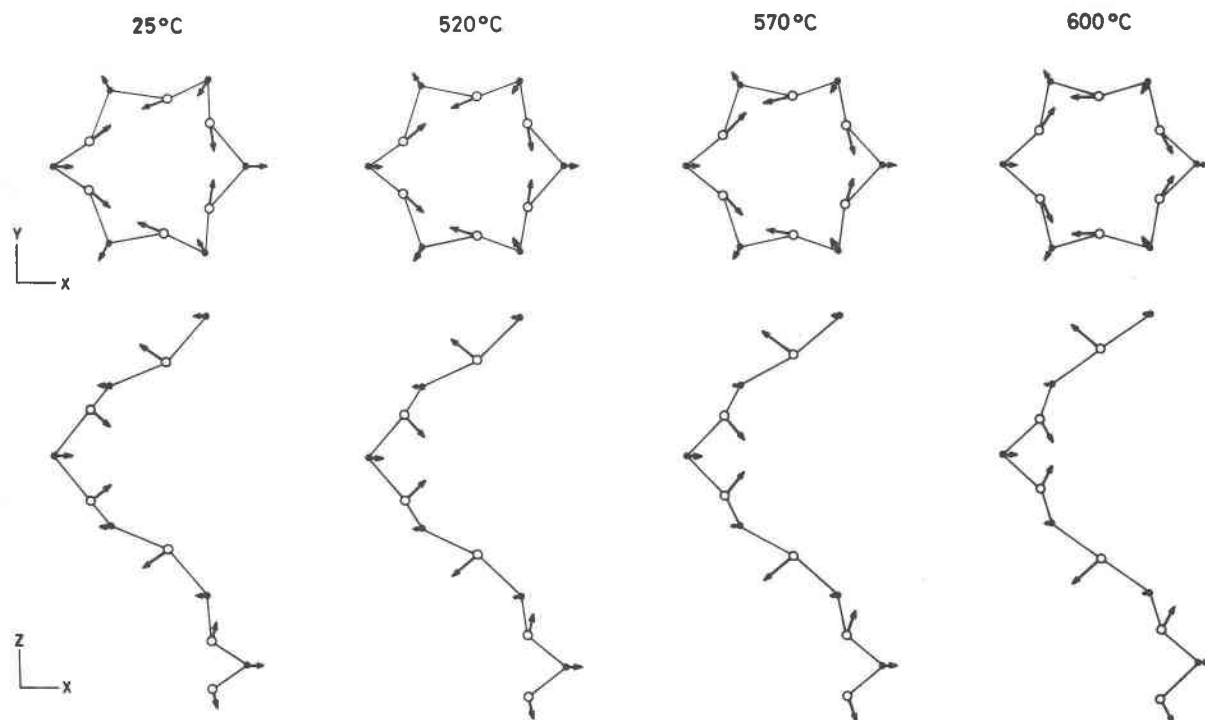


FIG. 1. Cartesian displacements for the soft mode  $A_1$ ,  $207\text{ cm}^{-1}$  modes of quartz at 25, 520, 570, and  $600^\circ\text{C}$ . Small black circles and large open circles indicate silicon atoms and oxygen atoms, respectively.

the  $207\text{ cm}^{-1}$  soft mode approaches zero as the transition temperature is approached from below. The observed values of this mode listed in Table 2 were estimated from Figure 1 of Höchli and Scott's paper. To confirm the gradual shift of this mode to lower frequencies with increasing temperature (up to the transition temperature), the internal rotation potential  $Y$  should be negative, as shown in Table 3. The internal rotation potential should be zero in  $\beta$  quartz, otherwise the soft mode  $207\text{ cm}^{-1}$  does not approach zero at transition point. If the same force field is assumed for  $\alpha$  and  $\beta$  quartz, the calculated frequencies for the soft mode with increasing temperature are larger than the observed frequencies, particularly in  $\beta$  quartz.

#### Vibrational Modes and Intensities

The normal modes have been represented by the Cartesian displacements  $n_k^\alpha$  of the atoms  $\alpha$  for each vibrational frequency  $k$ . They were normalized in order to satisfy the condition

$$\sum_{\alpha} m^{\alpha} n_k^{\alpha} n_l^{\alpha} = m_k \delta_{kl}, \quad (1)$$

where  $m^{\alpha}$  is the mass of an  $\alpha$  atom and  $m_k$  is an arbitrary positive constant, considered as the mass of

the mode  $k$ . Most of the modes, except the  $207\text{ cm}^{-1}$  mode, are little modified by the  $\alpha$ - $\beta$  structural change as reported by Etchepare *et al* (1974). Figure 1 shows the  $207\text{ cm}^{-1}$  vibrational mode at various temperatures. The atomic displacement of this mode at  $25^\circ\text{C}$  is in agreement with that of Etchepare *et al*'s Figure 2 (1974). As is clear from Figure 1, the vibrations of the  $207\text{ cm}^{-1}$  mode which rotate around the screw  $C_3$  become more in agreement with displacements involved in the  $\alpha$ - $\beta$  phase transitions, as the transition temperature  $T$  is approached from below. To make clearer the temperature-dependence of the soft  $207\text{ cm}^{-1}$  mode, the eigenvectors for this mode obtained from a lattice dynamical calculation at various temperatures were compared with spontaneous displacements associated with  $\alpha$ - $\beta$  phase transition. Table 6 shows the normal modes of soft  $207\text{ cm}^{-1}$  mode in Cartesian form. From these normal modes, the symmetry mode vectors were calculated with reference to Axe and Shirane's Figure 6 and Table 1 (1970). The results are listed in Table 7 together with the displacements in the  $\alpha$ - $\beta$  phase transition. This result demonstrates a remarkable temperature dependence of this soft mode and a remarkable similarity between this soft mode and the displacements involved in the  $\alpha$ - $\beta$  phase transition.

TABLE 6. Normal Mode of 207  $\text{cm}^{-1}$  Soft Mode in Cartesian Form\*

Atom		$\alpha$ quartz			$\beta$ quartz
		25°C	520°C	570°C	600°C
Si(1)	x	-0.263	-0.203	-0.187	-0.184
	y	0.456	0.351	0.325	0.319
	z	0.	0.	0.	0.
Si(2)	x	0.527	0.406	0.375	0.368
	y	0.	0.	0.	0.
	z	0.	0.	0.	0.
Si(3)	x	-0.263	-0.203	-0.187	-0.184
	y	-0.456	-0.351	-0.325	-0.319
	z	0.	0.	0.	0.
O(1)	x	0.603	0.541	0.500	0.366
	y	0.467	0.513	0.543	0.634
	z	0.465	0.584	0.611	0.622
O(2)	x	0.603	0.541	0.500	0.366
	y	-0.467	-0.513	-0.543	-0.634
	z	-0.465	-0.584	-0.611	-0.622
O(3)	x	-0.706	-0.715	-0.720	-0.732
	y	0.289	0.212	0.162	0.
	z	0.465	0.584	0.611	0.622
O(4)	x	0.103	0.174	0.220	0.366
	y	0.756	0.725	0.704	0.634
	z	-0.465	-0.584	-0.611	-0.622
O(5)	x	0.103	0.174	0.220	0.366
	y	-0.756	-0.725	-0.704	-0.634
	z	0.465	0.584	0.611	0.622
O(6)	x	-0.706	-0.715	-0.720	-0.732
	y	-0.289	-0.212	-0.162	0.
	z	-0.465	-0.584	-0.611	-0.622

\* The normalization was chosen to make the mass of Equation (1) equal to 100 atomic weight units.

As mentioned by Etchepare *et al* (1974) and Mirgorodskii and Lazarev (1973), a calculation of the intensities in the infrared spectrum of a crystal, using the two-charge model of Kleinman and Spitzer (1962), is useful as a means of checking the correctness of the results of the calculated normal modes. When the normal modes  $n_k^\alpha$  are known, the intensities are given by

$$S_k^{\text{calc}} = \left( \sum_{\alpha} B^{\alpha} n_k^{\alpha} \right) \left( \sum_{\alpha} B^{\alpha} n_k^{\alpha} \right), \quad (2)$$

where the tensor  $B^{\alpha}$ , the effective charge for atom  $\alpha$ , is determined using the scheme of Kleinman and Spitzer (1962). The covalent and ionic properties of quartz may be expected to give rise to two distinct kinds of effective charges, which are conveniently designated ionic and valent charges. According to Kleinman and Spitzer, the tensor for the ionic charges is

$$B_{\text{Si}}^{\text{ionic}} = e q I \text{ and } B_{\text{O}}^{\text{ionic}} = -\frac{1}{2} e q I, \quad (3)$$

where  $e$  is the electronic charge and  $I$  an unit matrix; and that for the valent charge is

$$B_{\text{Si}}^{\text{valent}} = -eQ \sum^{(\alpha)} \rho \rho \quad (4)$$

and

$$B_{\text{O}}^{\text{valent}} = eQ \sum^{(\alpha)} \rho \rho,$$

 TABLE 7. Symmetry Mode Vectors and Displacements in the  $\alpha$ - $\beta$  Phase Transition\*

Atom	Position in $\beta$ phase	General displacement				
Si(1)	$(0, \frac{1}{2}, 0)$	$(0, S_1, 0)$				
Si(2)	$(\frac{1}{2}, 0, \frac{1}{3})$	$(S_1, 0, 0)$				
Si(3)	$(\frac{1}{2}, \frac{1}{2}, -\frac{1}{3})$	$(-S_1, -S_1, 0)$				
O(1)	$(-x, x, \frac{1}{6})$	$(S_2+S_4, S_2-S_4, -S_3)$				
O(2)	$(-2x, -x, \frac{1}{2})$	$(2S_4, -S_2+S_4, S_3)$				
O(3)	$(-x, -2x, -\frac{1}{6})$	$(-S_2+S_4, 2S_4, -S_3)$				
O(4)	$(x, -x, \frac{1}{6})$	$(S_2-S_4, S_2+S_4, S_3)$				
O(5)	$(2x, x, -\frac{1}{2})$	$(-2S_4, -S_2-S_4, -S_3)$				
O(6)	$(x, 2x, -\frac{1}{6})$	$(-S_2-S_4, -2S_4, S_3)$				
Symmetry coordinates of 207 $\text{cm}^{-1}$ mode						
	Model calculation deduced from a lattice dynamical calculation (present work)			Inelastic neutron scattering (Axe and Shirane)	Spontaneous displacements associated with $\beta \rightarrow \alpha$	
	25°C	520°C	570°C	600°C		
$S_1/S_2$	0.75	0.57	0.53	0.50	0.54( $\pm 0.17$ )	0.490( $\pm 0.019$ )
$S_3/S_2$	-0.66	-0.82	-0.87	-0.85	-0.80( $\pm 0.05$ )	-0.802( $\pm 0.037$ )
$S_4/S_2$	0.24	0.17	0.13	0.00	0.28( $\pm 0.06$ )	0.013( $\pm 0.052$ )

\* Expressed in hexagonal coordinates with  $x = 0.2068$ .

TABLE 8. Comparison of Observed and Calculated Infrared Intensities for the  $A_2$  and  $E$  Frequencies

Symmetry	Frequency	$S_k^{\text{exptl}}$	$S_k^{\text{calc}}$	
			Present work $q=2.70, Q=2.88$	Etchepare <i>et al.</i> results $q=2.5, Q=2.75$
$A_2$	1080	180	178	178
	778	14	0.6	0.1
	495	37	38	29
	364	21	25	17
$E$	1162	1	0.7	3
	1072	167	165	178
	795	16	1.2	0.2
	697	2	1.1	0.1
	450	38	47	36
	395	12	6	5
	265	3	3	1
	128	0.2	0.1	0.2

where the sum has to be made over all the unit neighbor vectors of atoms.

The experimental values  $S_k^{\text{exp}}$  of Spitzer and Kleinman (1961) and the calculated values  $S_k^{\text{calc}}$  of ours and of Etchepare *et al* (1974) are listed in Table 8. Both calculated results account for the intensities of infrared absorption, as well for the  $E$ -type modes as for the  $A_2$ -modes. This result shows that the normal modes calculated on the basis of modified Urey-Bradley force field are correct as well as those modes calculated on the basis of the valence force field.

### Conclusions

The Urey-Bradley force field modified by the terms of the bond interaction potential  $p$  and the internal rotation potential  $Y$  accounts for the observed infrared and Raman active frequencies of  $\alpha$  and  $\beta$  quartz to a good approximation. The internal rotation potential  $Y$  is the most important force constant for the  $207\text{ cm}^{-1}$  soft mode. The value of this force constant is negative during the  $\alpha$ - $\beta$  phase transition, suggesting that the displacement parameter in quartz consists of the internal rotation and that this displacement occurs easily during the  $\alpha$ - $\beta$  phase transition, and never occurs in the case of  $\beta$  quartz.

The vibrational mode at  $207\text{ cm}^{-1}$  rotates around the screw  $C_3$ . This vibrational mode becomes more in agreement with displacements during the  $\alpha$ - $\beta$  transition when the transition temperature  $T$  is approached from below.

The two-charge model of Kleinman and Spitzer was used to derive the infrared intensities for the  $A_2$ -

and  $E$ -type modes. The agreement between the calculated and observed intensities shows the correctness of the normal modes determined in this work.

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