FIG. 2. (A) Plot of tetrahedra SiO stretching vibration vs mole% of Na$_2$O. (B) Plot of terminal SiO stretching vibration vs mole% of Na$_2$O. (C) Plot of SiOSi stretching vibration vs mole% of Na$_2$O. (D) Plot of bending vibrations vs mole% of Na$_2$O.

In pressure studies made on α-quartz, fused silica, Vycor, and Pyrex glasses, the pseudolatticelike Si stretching mode at ~800 cm^{-1} was found to be most pressure dependent. [10] For the sodium silicate glasses, all of the vibration modes studied are pressure sensitive, especially the tetrahedral Si-O stretching (~1100 cm^{-1}) and the bridging Si-O-Si stretching (~790 cm^{-1}) modes, and the terminal Si-O stretching (~960 cm^{-1}) mode. The effect of Na$_2$O on $d\nu_i/dP$ appears to be greater than the effect of B$_2$O$_3$ on $d\nu_i/dP$ in Vycor and Pyrex glasses. Differences between the effects of B$_2$O$_3$ and Na$_2$O on $d\nu_i/dP$ in silicate glasses are not unexpected since B$_2$O$_3$ is a glass former and strengthens the glass (e.g., elastic moduli increase as B$_2$O$_3$ increases), [1,2] whereas Na$_2$O is a glass modifier and weakens the glass.

The mode Grüneisen γ, γ_i, in Table III are evaluated from the relation

$$\gamma_i = \frac{K_T}{\nu_i}\left(\frac{d\nu_i}{dP}\right), \tag{1}$$

where K_T is the isothermal bulk modulus.

Whenever comparisons are possible, the sodium silicate glasses demonstrate γ_i values which are higher than those calculated for α-quartz and other silicate glasses, [10] and in every case are positive. The α-quartz and fused silica glass demonstrate negative γ_i values for some modes and also show anomalous thermal expansion and elastic behavior. [10,19] The positive γ_i values for the sodium silicate glasses are consistent with the effects of network filling agents such as Na$_2$O in diminishing these anomalies. [20] The higher ionic character of the sodium silicate glasses is also contributory to the higher sensitivity to pressure as opposed to the pure silicate glasses or those incorporating the more covalent boron atoms into the glass framework. [1,21,22]

Contrary to what was found for α-quartz and other silicate glasses, [10] even the modes involving the motions of the atoms within the SiO$_4$ tetrahedra in the sodium silicate glasses are significantly pressure sensitive. Thus, with an increase in pressure, the sodium silicate glasses demonstrate compression along the intertetrahedral linkages, but in addition some distortions of the individual tetrahedra[20] must occur. This difference from α-quartz and related nonmodified silicate glasses must relate to the insertion of the modifying sodium ions in the interstices of the glasses.

B. Thermal expansion and the Grüneisen parameters

The observed negative thermal expansion coefficients, α_v, at $T < 200$ °K for fused silica and Pyrex and the effects of diminishing this anomaly by the addition of a network filling agent such as Na$_2$O is of considerable interest. [23,24] The coefficient, α_v, is related to $\bar{\gamma}_{th}$ through the relation

$$\bar{\gamma}_{th} = \alpha_v K_s/\rho C_v, \tag{2}$$

where K_s is the adiabatic bulk modulus, ρ and C_v are density and specific heat at constant volume. $\bar{\gamma}_{th}$ is also related to γ_i and C_{v_i} by the relationship

$$\bar{\gamma}_{th} = \sum_{i=1}^{3n} \gamma_i C_{v_i} \Big/ \sum_{i=1}^{3n} C_{v_i}, \tag{3}$$

TABLE III. Mode Grüneisen parameters calculated for various sodium silicate glasses.

| Glass (mole % Na$_2$O)	ν_i (cm^{-1})	$d\nu_i/dp$ (cm^{-1}/kbar)	χ (kbar^{-1})	Calculated γ_i
α-quartz(0)	783 800	0.14	0.002 67	0.07
Fused silica(0)	815	0.17	0.003 02	0.07
Vycor(0)	814	0.22	0.003 82	0.07
Pyrex(4)	812	0.27	0.002 89	0.12
(10)	787	0.64	0.002 95	0.28
(25)	765	0.50	0.002 70	0.24
(35)	755	0.48	0.002 52	0.25
(35.5)	760	0.50	0.002 53	0.26
(40)	750	0.50	0.002 51	0.27
(45)	730	0.56	0.002 32	0.33
α-quartz(0)	1082	−0.07	0.002 67	−0.02
(10)	1085	0.46	0.002 95	0.14
(25)	1065	0.45	0.002 70	0.16
(35)	1070	0.48	0.002 52	0.18
(35.5)	1075	0.50	0.002 53	0.18
(40)	1060	0.42	0.002 51	0.16
(45)	1040	0.42	0.002 32	0.17
(25)	975	0.45	0.002 67	0.17
(35)	940	0.35	0.002 52	0.15
(35.5)	940	0.50	0.002 53	0.21
(40)	935	0.40	0.002 51	0.17
(45)	935	0.45	0.002 32	0.21
α-quartz(0)	459	0.09	0.002 67	0.07
Fused silica(0)	475	−0.07	0.003 02	−0.05
(10)	460	0.19	0.002 95	0.14
(25)	462	0.13	0.002 70	0.10
(35)	458	0.16	0.002 52	0.14
(35.5)	458	0.21	0.002 53	0.18
(40)	460	0.13	0.002 51	0.11
(45)	468	0.19	0.002 32	0.18
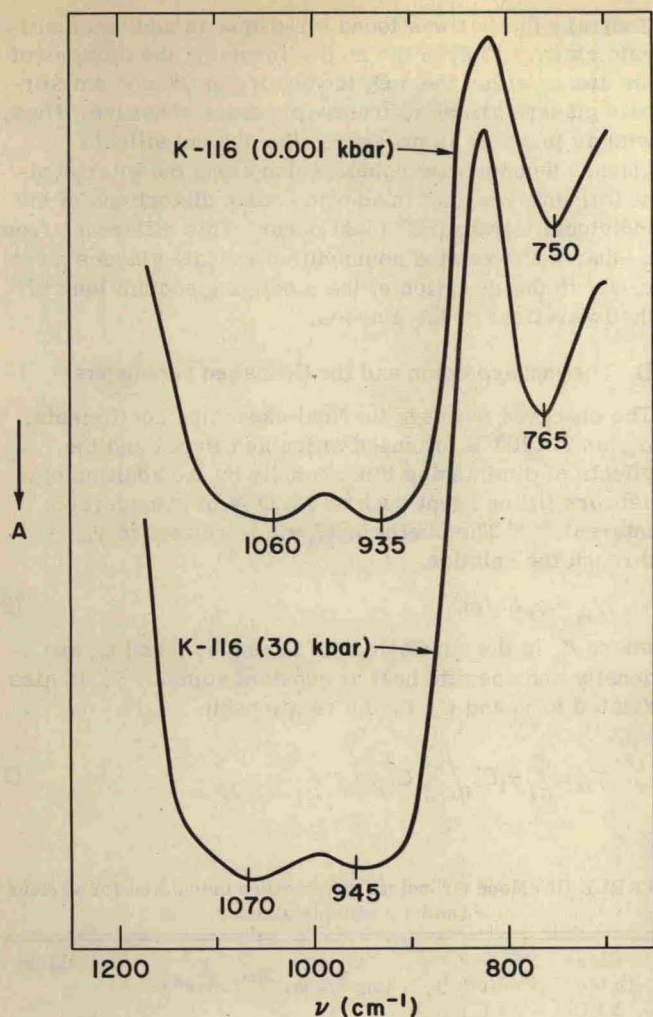
FIG. 3. Spectra of the K-116 glass at varying pressures from 1200—700 cm^{-1}.

where γ_i is defined by Eq. (1) and C_v is the specific-heat contribution for each vibrational mode to the total Einstein specific heat.

Since the thermal expansion data were obtained at room temperature and above, we will consider only the high-temperature limit of $\bar{\gamma}_{th}$ designated as γ_{HT}. γ_{HT} may be calculated from the pressure derivatives of the elastic parameters, assuming only the acoustic modes contributing to γ;

$$\gamma_{HT} = \tfrac{1}{3}(\gamma_p + 2\gamma_s), \qquad (4)$$

where

$$\gamma_s = \frac{1}{3} + K_T\left(\frac{\partial \ln v_s}{\partial \ln P}\right)_T \qquad (5)$$

and

$$\gamma_p = \frac{1}{3} + K_T\left(\frac{\partial \ln v_p}{\partial P}\right)_T . \qquad (6)$$

Here γ_p and γ_s are the γ contributions to the compressional and shear-wave propagation, and v_p and v_s represent, respectively, compressional and shear acoustic wave velocities.[25,26]

Table IV shows a comparison of $\bar{\gamma}_{th}$ and γ_{HT} for the sodium silicate glasses at 298 °K. The values for α-quartz, fused silica, Vycor, and Pyrex are also included. We have no ready explanation for the observed differences in the $\bar{\gamma}_{th}$ and γ_{HT} values.

It is significant to note that as the Na$_2$O content increases, the optical γ_i values are observed to increase (Table III). The $\bar{\gamma}_{th}$ parameter increases slightly, but the γ_{HT} values increase significantly, and are much more sensitive to compositional changes occurring in the glasses. It may also be observed that the negative γ_{HT} values are related to the anomalous behavior in α-quartz and fused silica, for as Na$_2$O enters the glass, γ_{HT} becomes increasingly more positive and the anomaly decreases. Since Raman-active modes have not been examined under pressure, definite conclusions were not possible. However, the positive pressure dependences of the infrared-active modes examined, correlated with the absence of any negative thermal expansion observed for sodium silicate glasses.

SUMMARY

Infrared absorption spectra of sodium silicate glasses vary systematically with composition and pressure. The following findings are noteworthy:

(i) The strong broad band at ~1100 cm^{-1} due to Si-O stretching within the tetrahedron splits; the frequencies of both of the resultant bands decrease with substitution of Na$_2$O in the structure. With an increase in pressure these bands show a shift toward higher frequency.

(ii) The frequency and intensity of the bridging Si-O-Si stretching mode at ~790 cm^{-1} decreases with an increase in Na$_2$O content. The frequency was found to increase with pressure.

(iii) The low-frequency band, due to Si-O-Si and O-Si-O bending modes, slightly increases in frequency with Na$_2$O content, and with increasing pressure.

(iv) All values of $d\nu_i/dP$ for the four optical vibrational modes examined are positive.

TABLE IV. Thermal and elastic data and the Grüneisen parameter values for the Na$_2$O-SiO$_2$ glasses.

(mole % Na$_2$O)	$\bar{\gamma}_{th}$	γ_{HT}
(10)	0.003	−1.35
(15)	0.004	−0.84
(20)	0.006	−0.31
(25)	0.007	−0.17
(27.5)	0.008	0.32
(30)	0.008	0.49
(33.1)	0.009	0.68
(35)	0.011	0.71
(35.5)	0.010	0.74
(39.6)	0.011	0.93
(40)	0.012	1.03
(45)	0.013	1.08
α-quartz(0)	0.69[a]	...
Fused silica(0)	0.04	−2.32
Vycor(0)	0.04	−1.80
Pyrex(4)	0.22	−1.80

[a]N. Soga, J. Geophys. Res. 72, 4227 (1967).