Influence of swelling stresses on the shift of Raman vibration peaks

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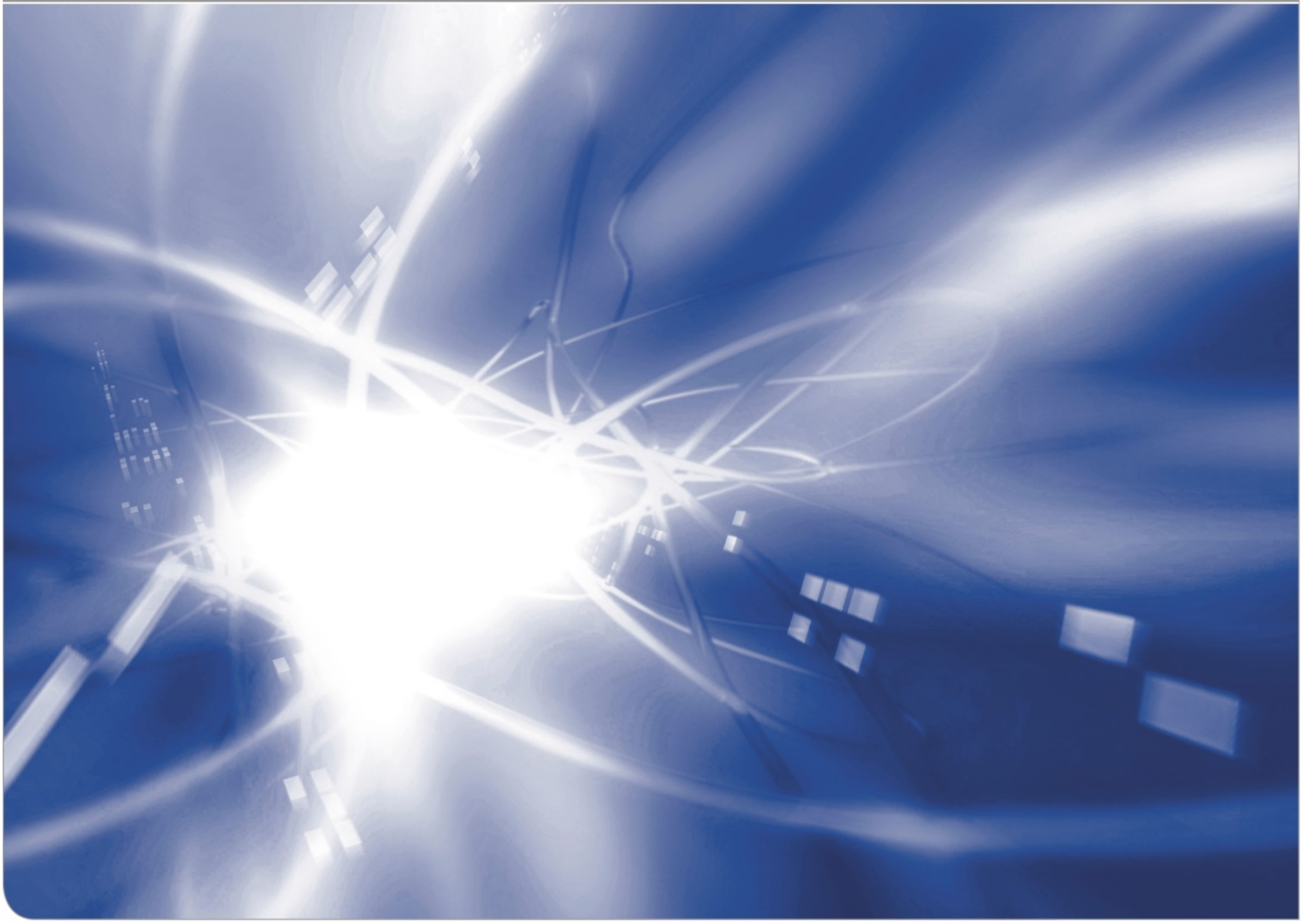

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Abstract

An interesting effect in silica glass is the shift of IR- and Raman-peaks under externally applied stresses. A first interpretation of the influence of stress on the IR frequency was made possible by its influence on the bond angles, as had been shown very early by Galeener [1]. In this interpretation, the stress effect is assumed as a consequence of a change of the bond angles due to the stresses.

In [2] we could show that the angle stretching is not the only effect that influences the position of the frequency of IR lines. For our computations we used the Lennard-Jones potential and could show that a tensile stress must result in a decrease of the frequency.

In the present report, we will show in which way also the water concentration in the surface region can affect the measurements via volume swelling due to the hydroxyl generation by the silica/water reaction.

Contents

1 Introduction

1.1 Some experimental results for the asymmetric stretching mode (AS)

An interesting effect in silica glass is the shift of IR- and Raman-peaks under externally applied stresses. The influence of uniaxial tensile stresses on the peak position of IR- and Raman-lines that has been measured by Tallant et al. [1], is shown in Fig. 1 with the peak position in terms of the wavenumber. These Raman-data were obtained in tensile test and the results are introduced as the red squares.

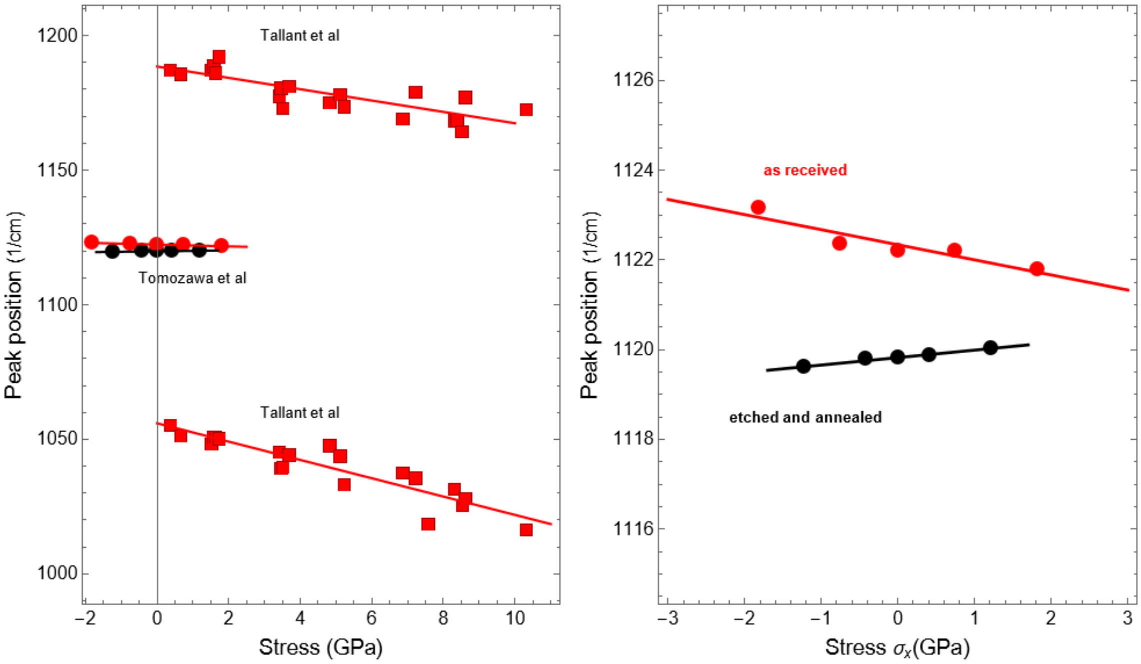

Fig. 1 Left: Measurements of Raman peak in the region of “asymmetric stretching (AS)” by Tallant et al. [1] on silica by uniaxial tensile tests (red squares). Data of IR-peak from bending tests by Tomozawa et al. [2] (red and black circles). Right: Data from [2] in higher resolution.

Measurements of the IR-peak in 2-point bending tests were performed by Tomozawa et al. [2]. The results for as-received fibres are introduced by the red circles. After annealing and etching away a surface layer of about 1 µm thickness, the measured data are shown by the black circles. The differences in the different surface states in Tomozawa et al. [2], as well as the strong deviations from the results of Tallant et al. [1], suggest that further surface state-dependent effects must be present.

The peak position (in the following abbreviated by *P* in terms of 1/cm) for uniaxial tension σ_x (in GPa) was found for the measurements by Tallant et al.[1]:

$$P = 1188 - 2.11\,\sigma_x \tag{1}$$

and

$$P = 1056 - 3.40\,\sigma_x \tag{2}$$

From the 2-point bending tests by Tomozawa et al. [2] (red circles in Fig. 1) we find

$$P = 1122.3 - 0.336\,\sigma_x \tag{3}$$

and for the case of surface-etched and annealed specimens (black circles in Fig. 1)

$$P = 1119.8 + 0.166\,\sigma_x \tag{4}$$

1.2 Theoretical interpretations for the asymmetric stretching mode

A first interpretation of the influence of stress on the IR frequency was made possible by its influence on the bond angles, as had been shown very early by Galeener [3]. In this interpretation, the stress effect is assumed because of a change of the bond angles due to the stresses.

In [4] we could show that the angle stretching is not the only effect that influences the position of the frequency of IR lines. For our computations, we used the Lennard-Jones potential and could show that a tensile stress must result in a decrease of the frequency. We therefore suggest using the following linear approximation up to an applied stress of around σ_{appl}/σ_0=0.4:

$$\frac{\alpha}{\alpha_0} \cong 1 - \frac{147}{169}\left(\frac{7}{13}\right)^{1/6} \frac{\sigma_{appl}}{\sigma_0} \tag{5}$$

where σ_{appl} is the applied stress, σ_0 the theoretical strength, and α_0 the spring constant in the absence of stresses. We prefer here the notation α for the spring constant according to Galeener [3], because the equilibrium constant for the hydroxyl reaction in Section 3 is usually noted by k. The “spring constant” α and the vibration frequency ν are related by

$$\nu = \sqrt{\frac{\alpha}{m}} \tag{6}$$

where m is the “reduced molecule mass”.

In the present report, we will show in which way also the water concentration in the surface region can affect the measurements via volume swelling due to the hydroxyl generation by the silica/water reaction.

2 Hydroxyl concentration at the surface

A glass fiber of radius r_0 is considered in Fig. 2 with all dimensions much larger than the water diffusion zone. The blue lines illustrate the water concentration C_w as a function of the depth z under the surface. The distribution of the total water concentration C_w in depth direction z is often given by an error-function

$$C_w = C_{w0}\,\mathrm{erfc}\left(\frac{z}{2b}\right) \tag{7}$$

with diffusion depth

$$b = \sqrt{Dt}\,, \tag{8}$$

surface concentration C_{w0}, the diffusion constant D, and the time t for the duration of the diffusion process. For approximate computations, the water distribution may be expressed as

$$C_w = \begin{array}{ll} C_{w0} & \mathit{for}\ z \le b' \\ 0 & \mathit{for}\ z > b' \end{array} \tag{9}$$

with
$$b' = \frac{2}{\sqrt{\pi}}\,b\,, \tag{10}$$

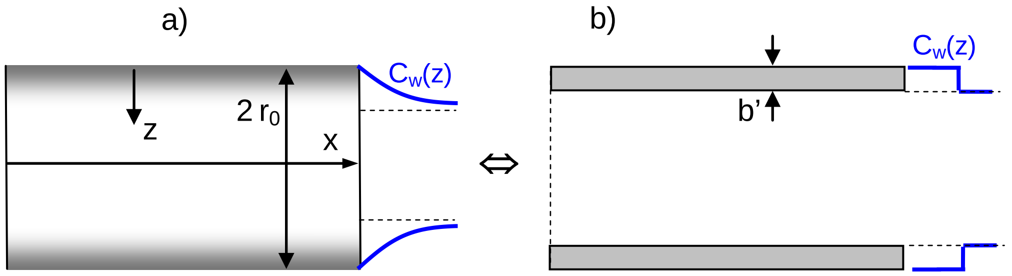

Fig. 2 Surfaces of silica fibres affected by water; a) water concentration $C_w(z)$ described by eq.(7), b) C_w(z) given by a simplified relation according to eq.(9).

3 Hydroxyl concentrations and swelling stresses

3.1 Basic relations

In *molar units*, the total water concentration is given by

$$C_w = C + \tfrac{1}{2}S = C(1 + \tfrac{1}{2}k) \tag{11}$$

where the quantity k is the equilibrium constant describing the ratio of $k=S/C$. The experimental results on equilibrium ratios from literature were expressed in [5] for the temperature range of $90°\mathrm{C} \le T \le 350°\mathrm{C}$ by the empirical relation

$$k = \frac{S}{C} = A\exp\left(-\frac{Q}{RT}\right) \tag{12}$$

(A=32.3 and Q=10.75 kJ/mol). If mechanical hydrostatic stresses σ_h are present, eq.(12) reads

$$k = \frac{S}{C} = A \exp\left(-\frac{Q - \sigma_h \Delta V}{RT} \right) = k_0 \exp\left(\frac{\sigma_h \Delta V}{RT} \right) \tag{13}$$

with the equilibrium constant k_0 in the absence of hydrostatic stresses. To simplify the description of possible time effects, it is assumed that the reaction rate is so high that the final reaction state is reached immediately during the mechanical loading.

Equations (11) and (12a) result in

$$S = \frac{C_w}{\left(\frac{1}{2} + \frac{1}{k} \right)} \tag{14}$$

and in *mass units* considering the slightly different mole masses of water and hydroxyl

$$S = \frac{17}{18} \frac{C_w}{\left(\frac{1}{2} + \frac{1}{k} \right)} \tag{14a}$$

The volume strain reads in terms of hydroxyl mass [6]:

$$\varepsilon_v = \kappa \times S \tag{15}$$

with the coefficient of proportionality

$$\kappa = 0.97 \;\; [0.92, 1.02] \tag{16}$$

The brackets in (16) stand for the 90% Confidence Interval. At a free surface, the stress state is *plane stress* and, consequently, also stresses caused by swelling are equi-biaxial (σ_x=0)

$$\sigma_{sw,y} = \sigma_{sw,z} = -\frac{\varepsilon_v E}{3(1-\nu)} \tag{17}$$

The swelling stresses at the glass surfaces are given by eqs.(15) and (17) as

$$\sigma_{sw,z} = \sigma_{sw,y} = -\kappa \frac{E}{3(1-\nu)} S \cong -28 \text{ GPa} \times S \tag{18}$$

In eq.(17) E=72 GPa is Young's modulus and ν=0.17 is Poisson's ratio. Consequently, the hydrostatic stress term reads

$$\sigma_{sw,h} = \tfrac{1}{3}(\sigma_{sw,y} + \sigma_{sw,z}) = -\frac{2\,\varepsilon_v E}{9(1-\nu)} \tag{19}$$

Introducing the proportionality (15) in (17) gives

$$\sigma_{sw,h} = -\underbrace{\frac{2\,\kappa E}{9(1-\nu)}}_{\lambda} S = -\lambda \times S \tag{20}$$

with the coefficient λ=18.7 GPa. Let us express eq.(14) in the form

$$\frac{1}{k} = \frac{C_w}{S} - \frac{1}{2} \tag{21}$$

Taking into account that the total swelling stress is the superposition of an applied axial stress and the swelling term

$$\sigma_h = \sigma_{appl,h} + \sigma_{sw,h}\ , \quad \sigma_{appl,h} = \sigma_{appl}/3 \tag{22}$$

we obtain an implicit equation between the swelling stress and the applied one. This fact can already be concluded from eq.(21), since the left-hand side with 1/*k* depends on the hydroxyl water content *S*. This holds also for the right-hand side, that contains *S* explicitly.

3.2 Solution of the implicit equation

There are different methods known to solve such an equation. As an example we will mention here the Mathematica-Routine FindRoot [7] that yields S=f(σ_{appl}). A graphical method is the computation of the inverse solution σ_{appl}=f(S) and then changing the coordinates. Here we apply this graphical procedure.

The equations (13), (18), (20), (21), and (22) result in

$$\sigma_{appl} = 3\lambda S - 3\frac{RT}{\Delta V}\ln\left[\left(\frac{C_w}{S} - \frac{1}{2}\right)\right] \tag{23}$$

Figure 3a shows the applied axial stress σ_{appl} as a function of the hydroxyl concentration *S* for a total water concentration of C_{w}=0.001. In Fig. 3b, we changed the ordinate and the abscissa, now showing the concentration *S* as a function of the applied stress.

The swelling stress as a function of the applied axial one is illustrated in Fig. 3b. Finally, Fig. 3c shows the applied stress vs. the hydroxyl concentration *S*. This plot is equivalent to Fig. 3a. The result is rather trivial and indicates that the asymptotes of *S* agree with $2C_{\mathrm{w}}$.

The total stress, defined as the sum of externally applied axial stress and the axial component of the swelling stress, $\sigma_{\mathrm{sw,x}}$,

$$\sigma_{total,x} = \sigma_{appl,x} + \sigma_{sw,x} \Rightarrow \sigma_{total,x} \geq \sigma_{appl,x} \tag{24}$$

is shown in Fig. 4a for different water concentrations C_w in the range of $0 \leq C_w \leq 0.004$. For the direction of coordinate x, see Fig. 2a.

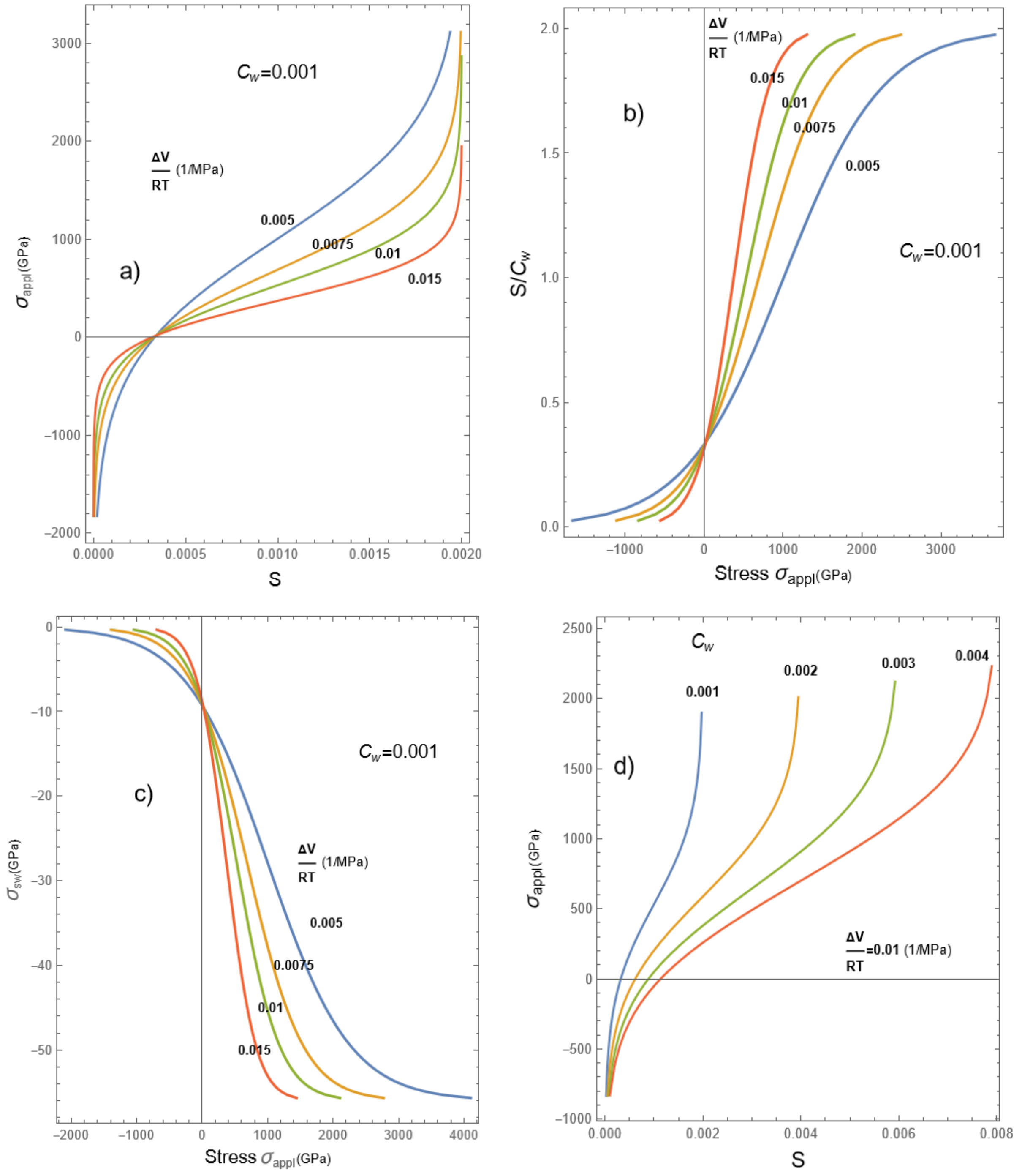

Fig. 3 a) Solution of eq.(23) for C_w=0.001, b) ordinate and abscissa changed, c) swelling stress as a function of the applied stress, d) effect of different maximum water concentrations at the surface.

Since the swelling stress is negative, the total stress is less the applied one. From eq.(10a) in [4], we can conclude for the frequency ν or the spring constant α that

$$\left(\frac{\nu}{\nu_0}\right)^2 = \frac{\alpha}{\alpha_0} \cong 1 - \frac{147}{169}\left(\frac{7}{13}\right)^{1/6}\frac{\sigma_{total,x}}{\sigma_0} \tag{25}$$

(α_0, ν_0=spring constant and frequency in the absence of swelling stresses).

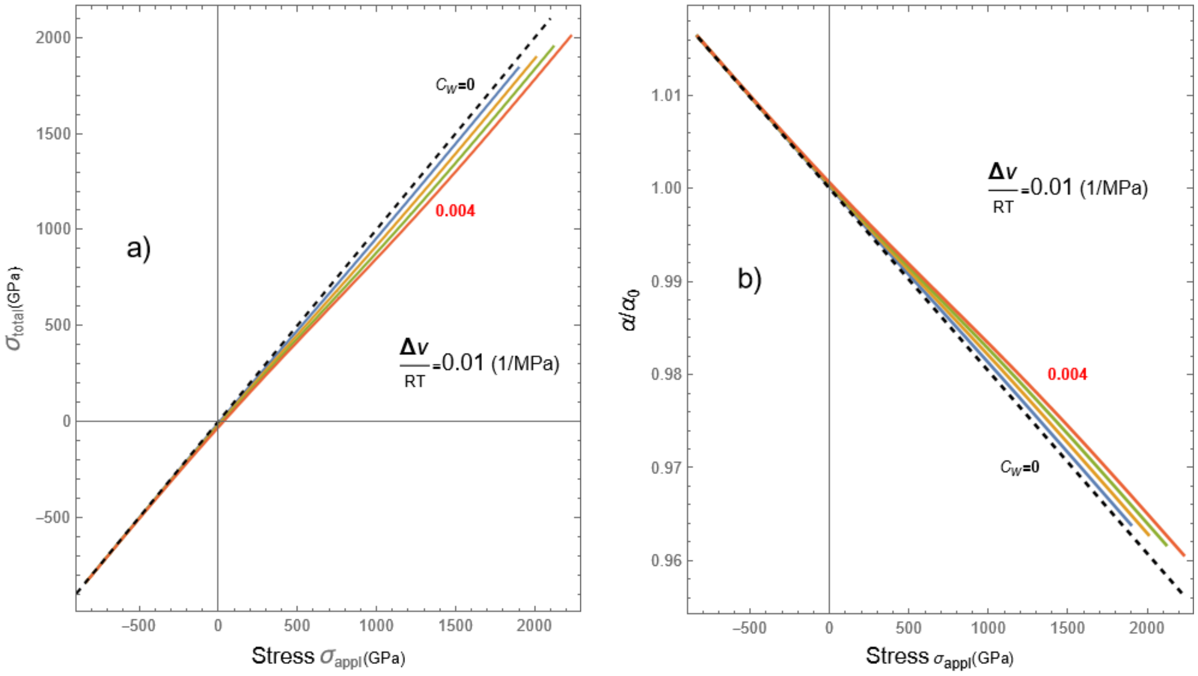

Fig. 4 a) Total stress σ_{total} as a function of the externally applied stress, b) effect of the local swelling stress on the spring constant α.

Conclusions

- The equilibrium constant $k=S/C$ of the water/silica reaction depends on the applied and the swelling stresses in a volume element.
- Since the swelling stresses are always negative, the peak position of Raman and IR-spectra under a superimposed axial tensile stress must increase due to eq.(25).
- For transmission measurements, the influence of the swelling stresses is negligible compared with that of the applied stresses, because the thickness dimension of the swelling zone is negligible compared to the fibre thickness.
- In contrast to transmission measurements, the local stress effect obtained in the reflection mode close to the surface can be expected to be significantly greater.

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