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Vibrational properties of siloxene: isotope substitution studies

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Abstract

The vibrational properties (IR and Raman) of the two-dimensional sheet polymer siloxene ($Si_6O_3H_6$) are studied using $^1H - ^2H$ and $^{16}O - ^{18}O$ substitution. While the stretching vibrations shift as expected under the substitution experiments, the low frequency bending vibrations shift anomalously. In particular, the lines previously attributed to a silicon phonon mode ($514\ cm^{-1}$ in IR and $496\ cm^{-1}$ in Raman) show the typical H–D isotope shift in IR, but appear to harden to $575\ cm^{-1}$ in Raman scattering. These results contain important information about the siloxene microstructure. © 1998 Elsevier Science B.V. All rights reserved

Keywords: Vibrational properties; Siloxene; Isotope substitution

1. Introduction

Due to the indirect band structure of silicon, this material cannot be used for light emitting devices. Alternative silicon-based materials with a direct band gap are low dimensional silicon polymers. Siloxene, a 2-d silicon–oxygen-compound with a direct band gap of approximately 2.5 eV was first prepared by Wöhler using a topochemical reaction [1]. The material consists of stacked Si planes, terminated by H and OH-groups. The distance between Si planes is 6.3 pm [2,3]. While Wöhler siloxene has been thoroughly characterised by X-ray diffraction, the vibrational properties of this material are still not fully understood. In particular, the microscopic origin of the $514\ cm^{-1}$ mode in as-prepared material and the $880\ cm^{-1}$ mode in annealed siloxene are still subject to discussion [4]. In the following, we investigate the vibrational properties of siloxene using isotope substitution with ^2H and ^{18}O, which lead to a more reliable assignment of the different IR and Raman modes.

2. Experimental results

2.1. Sample preparation

The siloxene samples studied were prepared by the conventional Wöhler method starting from $3 \times 3 \times 3\ mm^3$ $CaSi_2$ crystals. Deuterated siloxene was obtained using DCl in D_2O with an isotope enrichment of 99.5 at.%. ^{18}O substituted siloxene was prepared from 37% HCl in $H_2^{18}O$ solution made by exposing $H_2^{18}O$ (70% enrichment) to HCl gas.

2.2. Infrared spectra

The infrared transmission spectra generally change as expected under $^1H - ^2H$ substitution (Fig. 1a). In

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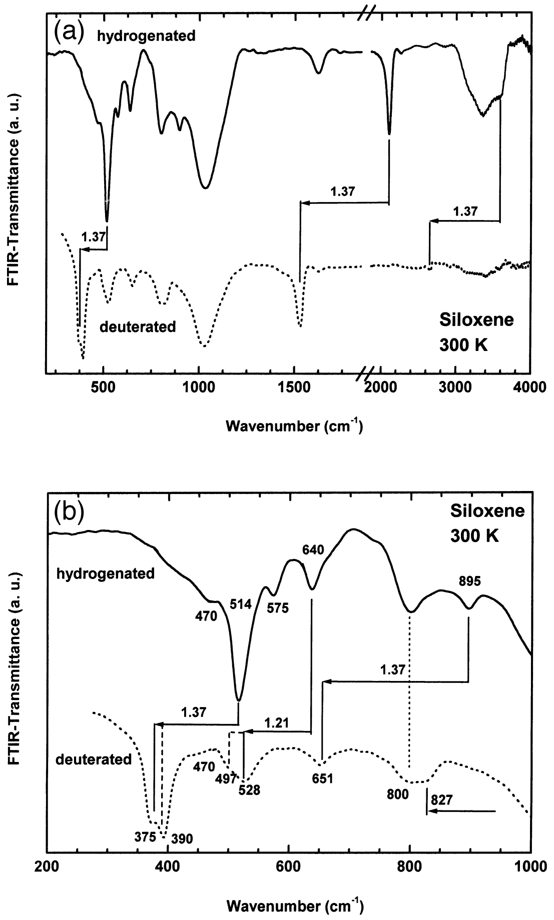

Fig. 1. (a) Infrared transmission spectra of siloxene prepared with HCl (full curve) and DCl (dotted curve), recorded at 300 K, (b) details of the low frequency region (200–1000 cm^{-1}).

particular, the sharp 2100 cm^{-1} SiH stretching mode shifts to 1530 cm^{-1} (i.e., by a factor 1.37, close to the value of 1.39 expected from the ratio of the Si–H and Si–D reduced masses). The SiH$_2$ scissors mode, probably arising from the disordered boundaries of the siloxene layers, shifts by the same factor, from 895 cm^{-1} to 651 cm^{-1}. In hydrogenated amorphous silicon it is well known that the Si–H bending at 640 cm^{-1} shows an anomalously low isotope shift by only a factor of 1.25 toward 520 cm^{-1}. This is due to a mode repulsion between Si–D vibrations and the Si lattice phonons (TO) [5]. A similar explanation can be used to describe the behaviour in siloxene (Fig. 1b), where we observe an isotope shift by a factor of 1.21. Note also that both Si–D related modes (375 and 528 cm^{-1}) exhibit a companion peak (390 and 497 cm^{-1}, respectively) not observed in hydrogenated siloxene. Again, this is indicative of a strong mode coupling between Si–D and the Si phonon background around 500 cm^{-1}. The line at 514 cm^{-1} in hydrogenated siloxene was previously attributed to silicon phonons [6], which become IR-active due to the different H- and OH-ligands at the silicon planes. In contrast to this model, the 514 cm^{-1} IR-line disappears upon deuteration and shifts to 375 cm^{-1} (factor 1.37). The additional modes observed in deuterated siloxene at 390, 497, and 528 cm^{-1} only appear after deuteration. However, they do not have such a straightforwardly corresponding mode in hydrogenated siloxene. The Si–O–Si stretching vibrations (asymmetric, 1034 cm^{-1}, and symmetric, 800 cm^{-1}) remain unchanged, as expected.

The assignment to Si–O modes can be verified by $^{16}O-^{18}O$ substitution. The Fourier transform infrared (FTIR) spectrum of ^{18}O-substituted siloxene is shown in Fig. 2. Due to the small mass difference between ^{16}O and ^{18}O and the incomplete isotope exchange, the changes induced in the spectra are relatively small. However, a clear shift of the asymmetric Si–O–Si stretching mode (from 1034 cm^{-1} to 1013 cm^{-1}) and the symmetric Si–O–Si mode (from 800 cm^{-1} to 787 cm^{-1}) is found, in accordance with [7]. The current assignments of the modes

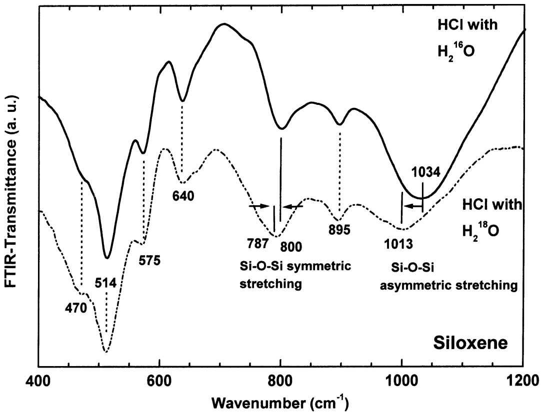

Fig. 2. Infrared transmission spectra of siloxene made with $H_2{}^{16}O$ (full curve) and $H_2{}^{18}O$ (dashed curve), recorded at 300 K. The oxygen unrelated modes are shown with dotted lines.

Table 1
Compilation of the assignment of the IR modes observed

Siloxene ^{1}H and ^{16}O ω (cm^{-1})	Siloxene ^{2}H substitution ω (cm^{-1})	Siloxene ^{18}O substitution ω (cm^{-1})	Assignment	Literature
3600	2652	3574	O–H-stretching	[8]
2250	1630		H–Si–O_3 stretching	[4]
2100	1530		H–Si–Si_3 stretching	[4]
1620			O–H bending	[9]
1034		1013	Si–O–Si asymmetric stretching	[7]
895	651		Si–H_2 scissors	[10]
800		791	Si–O symmetric stretching	[7]
640	528 and 497		Si–H bending	[5,10]
575			Si–H mode	
514	375 and 390		Si–H mode	[5,6]
470			Si–H mode	

after ^{1}H–^{2}H and ^{16}O–^{18}O substitution in siloxene are listed in Table 1.

2.3. Raman spectra

Complementary to the IR measurements, we have performed Raman spectroscopy on siloxene. The Raman spectra have been obtained with a He–Ne Laser (632.8 nm, 1 mW point focus) to avoid excitation of the luminescence of siloxene. Fig. 3a shows the room temperature Raman results. Partial ^{1}H–^{2}H substitution was used in these experiments by mixing HCl in H_2O and DCl in D_2O solutions in the given ratios. The top spectrum is that of siloxene prepared with HCl only. Not shown is the Si–H stretching mode at 2100 cm^{-1}, which shifts as expected to 1530 cm^{-1}. The relative intensity of the 2100 and 1530 cm^{-1} modes was used to check the H/D ratio in the samples.

The largest amplitude line in hydrogenated siloxene occurs at 496 cm^{-1}. Under H–D substitution, in contrast to the IR spectra, we observe a shift to larger reciprocal wavelength of the dominant mode to 575 cm^{-1}. Furthermore, from the partially substituted samples it becomes obvious that a continuous shift of this mode occurs during gradual deuteration. For comparison, the corresponding IR absorption spectra are shown in Fig. 3b.

A detailed inspection of Fig. 3, shows a rather complicated behaviour. The 496 cm^{-1} Raman mode shifts slightly to lower energies (~ 6 cm^{-1} at 50% D substitution) and decreases in intensity roughly proportional to the diminishing H-concentration.

No additional Raman-line at 362 cm^{-1} (factor 1.37) is observed, however. Instead, the shoulder at ~ 520 cm^{-1} in hydrogenated siloxene increases in intensity, shifts to higher energies and exhibits a doublet at about 50% D-substitution. In addition, both Raman and IR spectra show a nearly identical behaviour in the wave number region around 650 cm^{-1}. Here, additional lines at 657 cm^{-1} and 675 cm^{-1} appear under gradual deuteration, however disappear completely, including the initial 640 cm^{-1} mode, upon complete deuteration. We note that the Raman line at 380 cm^{-1} is the largest amplitude line in $CaSi_2$, which also contains 2-d Si planes as the prominent structural feature.

3. Discussion

We discuss the low frequency IR- and Raman-modes around 500 cm^{-1}. The intensity of the 514 cm^{-1} and 2100 cm^{-1} modes is comparable, as is observed for the 640 cm^{-1} and 2000 cm^{-1} bending and stretching modes in a-Si:H. This similarity could indicate that the proper assignment of the 514 cm^{-1} mode in hydrogenated siloxene is the SiH-bending mode. Indeed, this mode shows the proper shift (factor 1.37) under deuterium substitution. The additional line at 390 cm^{-1} could then be due to an interaction of this bending mode and a 380 cm^{-1} phonon of the silicon backbone (as observed in Raman). The remaining IR modes and the anomalous (negative) isotope shift observed in Raman are more difficult to understand. Due to the large number of modes present, it is highly likely that mode coupling occurs, which leads to this complicated behaviour both in the range of 500 to 575 cm^{-1} and 630 to 675 cm^{-1} under substitution. Theoretical calculations are clearly needed to resolve this anomalous behaviour, which in its strength has not been observed in other silicon-based systems before.

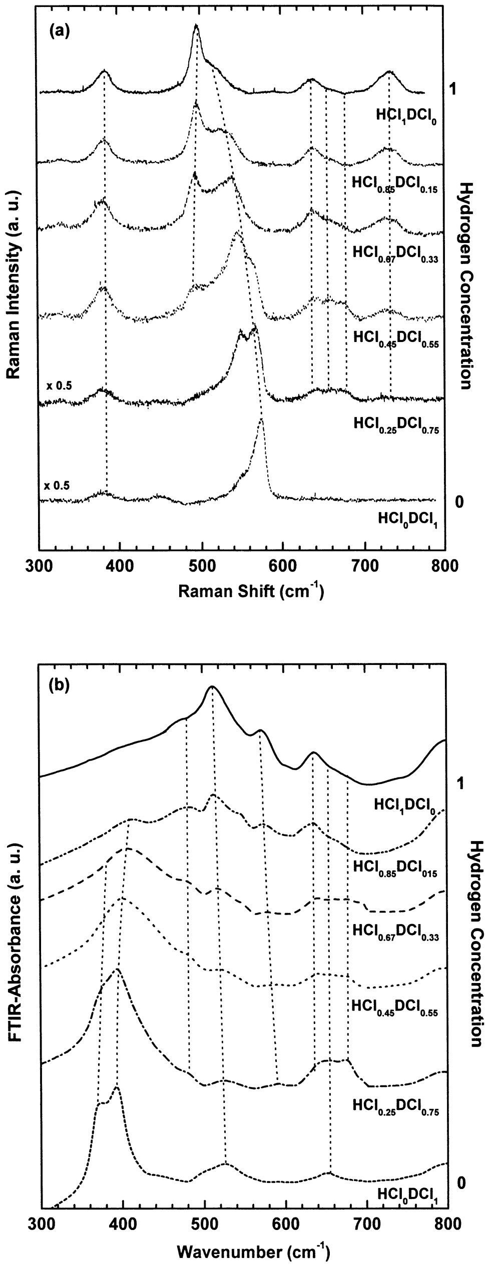

Fig. 3. (a) Room temperature Raman spectra of siloxene: The top spectrum is that of siloxene made with HCl only. Excitation by He–Ne Laser (632.8 nm). (b) Corresponding infrared absorption spectra of siloxene samples with different H–D substitution ratios.

4. Conclusion

We have investigated the changes in the IR and Raman spectra of siloxene induced by isotope substitution. While the IR spectra show the expected isotope shifts, the Raman spectra exhibit all anomaly in the range 500 to 575 cm^{-1} which requires both further theoretical and experimental investigations.

Acknowledgements

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