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Vibrational Anti-Crossing in Siloxene

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Siloxene, a two-dimensional sheet polymer, is essentially a three-dimensional stack of hydrogenated Si(111) surfaces. It can therefore act as a model system which allows to investigate the properties of this surface with bulk sensitive spectroscopy methods. We present here a comparative study of the vibrational properties of hydrogenated and deuterated siloxene using Raman scattering, FTIR spectroscopy and neutron scattering as well as force-constant modeling. A coupling of the Si–H bending mode and the in-plane Si phonon (both type E) is observed with all three experimental methods, but is most notable in Raman scattering, where the level anti-crossing results in an "anomalous" hardening of the dominant line from 496 cm^{-1} in hydrogenated to 575 cm^{-1} in deuterated siloxene. A coupling strength of 56 cm^{-1} is found, which is about 10% of the phonon energy.

The coupling of vibrational modes has been observed in a variety of semiconductor systems. Examples are the Fermi resonance observed between different local vibrational modes (LVM) of boron–deuterium and donor–hydrogen complexes in crystalline Si [1,2] or the coupling of the Se–H stretch mode with extended lattice phonons in AlSb [3]. In H–D isotope-substitution studies on amorphous hydrogenated silicon (a-Si:H), Cardona has noted an anomalously small softening of the Si–H bending mode upon deuteration, which he attributed to the interaction with phonons [4]. A similar coupling has been predicted for the hydrogenated Si(111) surface [5], however, has been difficult to verify experimentally until now.

Siloxene (or 2D-poly[1,3,5-trihydroxocyclohexasilane]) is a two-dimensional sheet polymer which is obtained via a topochemical reaction of $CaSi_2$ and HCl [6]. It consists of separated Si(111) planes with the fourth valence of each Si atom being saturated by H or OH groups. The resulting ideal structure shown in Fig. 1 essentially corresponds to a stack of Si(111):H surfaces. This material has a variety of interesting physical properties, most notably a direct band structure which leads to a highly efficient luminescence at 2.4 eV. Its vibrational properties have been studied by several groups [7 to 10], however, with an emphasis to identify the local vibrational modes. Here, we summarise our results of neutron and Raman scattering as well as Fourier-transform infrared (FTIR) absorption in hydrogenated and deuterated siloxene in the frequency range of 300 to 800 cm^{-1} which show a strong coupling of the Si–H bending mode with a phonon of the Si backbone.

The neutron-weighted density-of-states (DOS) for hydrogenated and deuterated siloxene obtained after correction for multiple phonon scattering is shown in the top of Fig. 2. Due to the high hydrogen and deuterium concentration and their significantly

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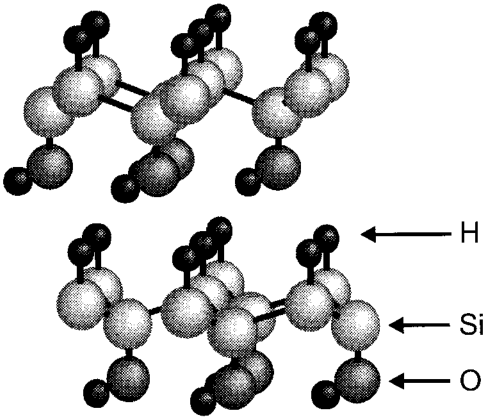

Fig. 1. Crystal structure of siloxene. The particular stacking of the adjacent planes shown corresponds to the tr6 modification

higher scattering cross sections compared to that of silicon, the DOS measured is dominated by the partial densities-of-states of H or D, respectively. In the relevant energy range, the DOS of hydrogenated siloxene shows a broad band with maxima at 550 and 640 cm^{-1}. The maximum at 640 cm^{-1} is caused by the Si–H bending mode and is seen in a-Si:H as well [11]. In contrast, the low-energy peak due to phonons is at least an order of magnitude stronger than in a-Si:H, which is a first indication that the motion of hydrogen atoms is involved in the phonon. Upon deuterium substitution, the DOS shifts to lower energies, with a ratio of the peak frequencies of ≈ 1.37, corresponding to the square root of the ratio of the reduced masses of Si–H and Si–D corrected for anharmonicity.

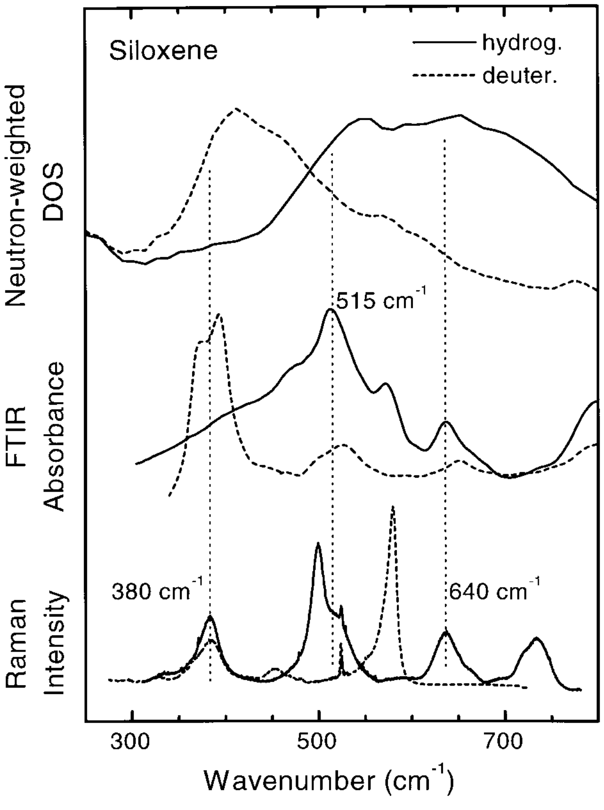

Fig. 2. Comparison of the neutron-weighted density-of-states, the Fourier-transform infrared absorbance and the Raman scattering intensity of hydrogenated and deuterated siloxene. All data have been normalised

The FTIR results in Fig. 2 show a similar behavior. In addition to the Si–H bending mode at 640 cm^{-1}, a broad absorption band with a maximum at 515 cm^{-1} is observed with FTIR in hydrogenated siloxene. This line was originally assigned to Si phonons which were assumed to become infrared active due to a dipole moment induced by the different electronegativities of the Si ligands H and OH [8]. In deuterated siloxene, a weak absorption band at 515 cm^{-1} is still found, which would be consistent with this model. However, the Si–D bending mode does not appear at the expected frequency of (640/1.37) cm^{-1} = 467 cm^{-1}. This has already been noted for a-Si:D, and has led to the postulation of the interaction with phonons mentioned above [4,12]. In contrast, a very strong absorption band at 380 cm^{-1} is observed in deuterated siloxene. Its position appears to be shifted by a factor of 1.36 from the 515 cm^{-1} mode, which on its own would indicate that both modes are simple H respectively D bending modes in contrast to the above model. The position of the dominant FTIR modes coincides with the steep increase of the respective DOS deduced from neutron scattering.

The clearest indication for an interaction between the Si–H bending mode and a Si-phonon comes from Raman scattering (bottom of Fig. 2). Again, in addition to the 640 cm^{-1} mode, Raman modes around 515 cm^{-1} are observed for hydrogenated siloxene: an intense narrow line at 496 cm^{-1} with a broad shoulder at ≈ 520 cm^{-1}. Upon deuteration, the spectrum changes drastically. Now, the narrow line is found at 575 cm^{-1}, with a weak shoulder towards lower frequencies. A weak Raman line is found at 450 cm^{-1} in deuterated siloxene only, while a strong Raman mode is observed at 380 cm^{-1} for both hydrogenated and deuterated siloxene.

The Raman results can be understood with the help of group-theoretical normal-mode analysis and force-constant modeling. An isolated siloxene plane has C_{3v}^1 symme-

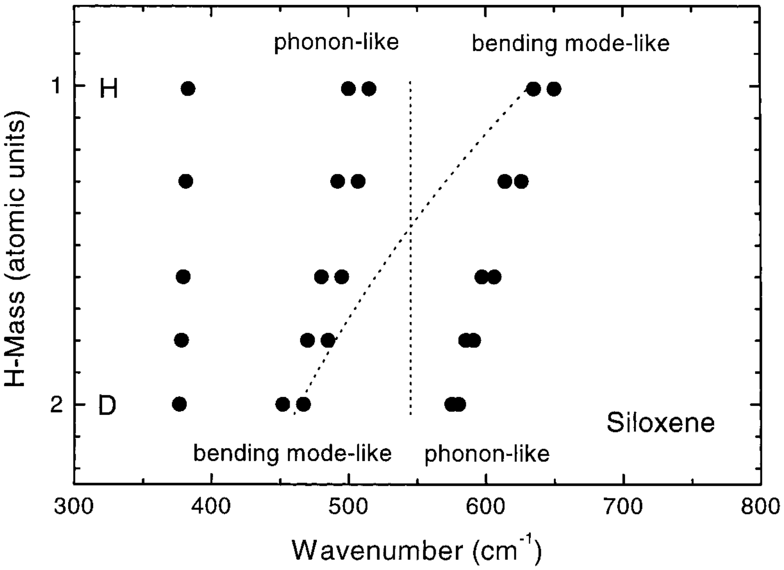

Fig. 3. Calculated mode frequencies for siloxene as a function of the hypothetical mass of the hydrogen atom using force-constant modelling. The dashed lines indicate the expected dependence when no interaction of the bending mode and the in-plane phonon would occur

try [9]. Two different optical Si-phonons, with the silicon atoms moving perpendicular to the siloxene plane (type A_1) and with the silicon atoms moving in the plane (type E), as well as the hydrogen bending mode (type E) are expected in this frequency region. Fig. 3 shows the respective mode positions as a function of the hypothetical mass of the hydrogen atom as predicted by force-constant modeling using the COMPASS parameterization [13]. At $\approx$380 cm^{-1}, the A_1 phonon mode is found, which is nearly independent of the hydrogen mass. At higher frequencies, the level anti-crossing between the E-modes is evident, their degeneracy being slightly lifted due to structure optimization. The theoretical predictions for hydrogenated and deuterated siloxene agree well with the observed Raman modes, including the shoulders discussed. In particular, the apparent hardening of the dominant Raman line can now be understood as the transition of the "phonon-like" mode from the low-frequency branch of the level anti-crossing in hydrogenated siloxene to the high-frequency branch in deuterated material.

In summary, we have shown that the layered structure of siloxene leads to vibrational properties which have been predicted for hydrogenated Si(111) surfaces [5]. We therefore have here a model system which allows the investigation of the properties of this surface with bulk-sensitive methods. Simple force-constant modeling can account for the level anti-crossing observed in siloxene for the long wavelength phonons at the Γ-point studied with Raman spectroscopy. However, more detailed calculations of the phonon dispersion will be necessary to fully describe the FTIR and neutron data presented.

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