

prevalence for prolate-shaped structures. A structural transition occurs at sizes around $n = 27$, however; larger clusters were found to prefer more spherical configurations (Jarrold and Constant, 1991). The preference for prolate shapes was attributed to a tendency of the silicon atoms to minimise coordination. This trend competes with the surface energy of the clusters, ultimately leading to a preference for spherical structural motifs in larger clusters (Jarrold and Constant, 1991). The experiments were repeated at higher resolution (Hudgins et al., 1999), and calculations confirm these experimental findings (Ho et al., 1998; Jackson et al., 2004).

Vibrational spectroscopy of anions has been performed by photoexcitation spectroscopy into the neutral state using electron detachment (Kitsopoulos et al., 1990; Xu et al., 1998). Comparison of the resultant spectral features with calculations reveals the structures of the anions. Recent work on larger silicon cluster anions reveals vibrational spectra indicative of the previously observed transition from prolate to spherical shapes (Meloni et al., 2004).

The FELIX free electron laser source provides intense and tunable infrared radiation including in the spectral range from 166 to 600 cm^{-1} where silicon clusters absorb. Vibrational spectroscopy of small silicon cluster cations was performed using multiple photon dissociation spectroscopy. The ions were analysed in a time-of-flight mass spectrometer. Also, isotopically selected ^{129}Xe atoms were attached to the clusters. Absorption of multiple IR photons would lead to a depletion of the ion signal, allowing the requisition of spectra of size-selected clusters. Comparison of the spectra with calculations using density functional theory revealed novel structures and a growth motif that started with a pentagonal bipyramid building block and changed to a trigonal prism for larger clusters (Lyon et al., 2009).

Related work provided information on the structure of small neutral sili-