Bond stiffness of ligand-protected metal clusters probed by X-ray absorption spectroscopy

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Metal clusters whose diameters are less than 2 nm exhibit specific thermal and temperature-dependent properties that are quite different from their bulk [1,2]. It was experimentally demonstrated that the size, morphology, and surface adsorbates affect the vibrational properties of the metal clusters [3]. Theoretical calculations predicted that the vibrational properties of the metal clusters depend on the geometric structure and composition [2,4]. However, atomistic level understanding of the effect of stiffness of intracluster bonds on thermal properties and stabilities has not been fully achieved so far and remains one of the primary goals for cluster research. Ligand-protected metal clusters whose geometrical structures have been determined by X-ray crystallography [5] provide us unique opportunity to study the correlation between structure and thermal stability. Recently, we revealed the hierarchy in bond stiffness in thiolate-protected gold clusters based on the analysis of temperature-dependent X-ray absorption fine structure (XAFS) data [6].

In the present study, we studied how the bond stiffnesses in metal clusters are affected by structural distortion and single-atom doping. To this end, ligand-protected Au clusters, $Au_{25}(SC_2H_4Ph)_{18}$, $[Au_{13}(dppe)_5Cl_2]Cl_3$, $Au_9(PPh_3)_8(PMo_{12}O_{40})$, $[Au_9(PPh_3)_8](NO_3)_3$, $[PdAu_8(PPh_3)_8]Cl_2$, were used as samples [5]. XAFS measurements were performed at BL01B1 of SPring-8. The stiffnesses of Au–Au(Pd) and Au–P(S,Cl) bonds within the clusters were evaluated by the analysis of the temperature dependence of Debye-Waller factors using Einstein model. The Au–Au bonds in the icosahedral Au_{13} core of $Au_{13}(dppe)_5Cl_2$ were stiffer than those of $Au_{25}(SC_2H_4Ph)_{18}$ due to higher symmetry for the former. The surface Au–Au bonds in the Au_9 core of $Au_9(PPh_3)_8(PMo_{12}O_{40})$ with a crown motif were stiffer than those of $Au_9(PPh_3)_8](NO_3)_3$ with a butterfly motif. The $PdAu_8$ core of $[PdAu_8(PPh_3)_8]Cl_2$ with a Pd-centered crown motif was more rigid than the Au_9 core of $Au_9(PPh_3)_8(PMo_{12}O_{40})$.

[1] M. Schmidt *et al*., *Nature*, **393**, 238-240 (1998).
[2] G.A. Narvaez *et al*., *Phys. Rev. B*, **72**, 155411 (2005).
[3] B.R. Cuenya *et al*., *Phys. Rev. B*, **84**, 245438 (2011).
[4] M.A. Ortigoza *et al*., *J. Phys. Chem. C*, **118**, 10335 (2014).
[5] T. Tsukuda, H. Häkkinen, *Protected Metal Clusters: from Fundamentals to Applications*, Elsevier (2015).
[6] S. Yamazoe *et al*., *Nat. Commun.*, **7**, 10414 (2016).