Strengthening of Au-Au bonds in small gold clusters by adsorbing noble gases LUCA M. GHIRINGHELLI, SERGEY LEVCHENKO, MATTHIAS SCHEFFLER, Fritz-Haber-Institut, D-14195, Berlin — In state-of-the-art experiments for the vibrational spectra of metal clusters in the gas phase, photodissociation spectroscopy is performed on clusters complexed with noble gas (RG) atoms, where a RG atom is usually expected to form a weak van der Waals bond. By employing DFT (PBE functional with selected comparisons to PBE0, and to MP2 and CCSD(T) calculations), we surprisingly find a partially covalent bond of neutral dimers with RG. For RG = Ar, Kr, Xe one or two RG atoms can bind in a linear molecule with Au$_2$. While both Hirschfeld and Mulliken analyses show a small electron transfer from the RG to Au$_2$, the Au-Au bond shortens and the Au-Au stretch frequency increases. This is inconsistent with the expected effect of electron transfer to the antibonding orbital of the dimer. Electron-density ($n_\text{e}$) differences between the bonded systems and the isolated fragments show an accumulation of $n_\text{e}$ between RG and the neighboring Au atom, and between the gold atoms. The analysis of the projected density of states reveals that, although only non-bonding orbital interactions and no charge transfer occurs between RG and Au$_2$, the $d$-electrons of Au$_2$ are redistributed due to the interaction with RG in such a way that the Au-Au $\sigma_s$ bond is strengthened.

Luca M. Ghiringhelli
Fritz-Haber-Institut, D-14195, Berlin

Date submitted: 11 Nov 2011

Electronic form version 1.4