Supporting information

Novel cage clusters of MoS$_2$ in the gas phase

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Supporting information 1

Figure 1.1 Schematic view of the sample spot on the MALDI target plate.
Supporting information 2

PSD mode spectra of some peaks

Figure 2.1. PSD spectrum of Mo$_3$S$_7^-$ (m/z=513) showing the fragments at Mo$_3$S$_4^-$ (m/z=417) and Mo$_3$S$_5^-$ (m/z=449).

Figure 2.2. PSD spectrum of Mo$_4$S$_6^-$ (m/z=574) showing fragment at Mo$_2$S$_3^-$ (m/z=285).
Figure 2.3. PSD spectrum of Mo$_{13}$S$_{28}^-$ showing the fragment ions, Mo$_{13}$S$_{26}^-$ (m/z 2081), Mo$_{13}$S$_{25}^-$ (m/z 2049) and Mo$_{11}$S$_{19}^-$ (m/z 1664).

Figure 2.4. Spectrum showing peaks due to MoO$_3$ and MoS$_2$ with clear isotope resolution.
Supporting information 3
Various analyses in the extracted MoS$_2$ flakes.

Figure 3.1. The infrared spectrum of the MoS$_2$ extract (a) is compared with bulk MoS$_2$ (b). There is a one to one correspondence between the peaks. Minor changes are attributed to the particle size effects (Maugea, F.; Lamotte, J.; Nesterenko, N. S.; Manoilova, O.; Tsyganenko, A. A.; Catalysis Today 2001, 70, 271–284).

Figure 3.2. UV-Visible spectrum of extracted MoS$_2$ nano flakes. The peak maximum is at 770 nm.
Figure 3.3. UV-Visible diffused reflectance spectrum of bulk MoS\textsubscript{2} showing the bulk band gap of 1.37 eV (Mattheiss, L. F.; Phys. Rev. Lett., 1973, 30, 784-787). The spike around 850 nm is due to a change in the light source of the instrument.

Figure 3.4 Raman spectrum of MoS\textsubscript{2} nanoflakes with 514 nm excitation. The spectrum was measured with a Witec confocal Raman microscope.
Supporting information 4

Figure 4.1. (A) Ion selection at m/z 162 corresponding to MoS$_2^-$, (B) ion selection at m/z 1146 corresponding to Mo$_8$S$_{12}^-$. While the first one shows extensive clustering, the other shows regular fragmentation. In both Mo$_{13}$ peak was not present.
Figure 5.1. Atomic structure of the Mo$_{13}$S$_{25}$ cluster. A cloud in the center is plotted as a complement of charge density (region where the density is very close to zero), clearly showing the void space enclosed inside the cage-like structure of the Mo$_{13}$S$_{25}$ cluster.
Figure 5.2. Charge density contours of the Mo$_{13}$S$_{25}$ cluster, viewed along z-axis (top view of the structure in Figure 1). Plane of the contours is chosen near the bottom triangle of Mo atoms such that it passes through both Mo-S and S-S bonds. Red and White colored rings centered on Mo atoms correspond to fully occupied semi-core 4s and 4p states. Angular contours near the Mo-S bonds indicate their mixed ionic and directional covalent character.
Figure 6.1. LDI spectrum of WS$_2$ showing magic clusters around the W$_6$ cluster. The W$_{12}$ and W$_{13}$ clusters are zoomed.

Figure 6.2. PSD mode LDI mass spectrum of W$_6$S$_9$O$^-$ showing no fragmentation. Inset: PSD of W$_{12}$S$_{20}$O$^-$ showing no fragmentation.