Supporting information

Novel cage clusters of MoS_2 in the gas phase

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Supporting information 1

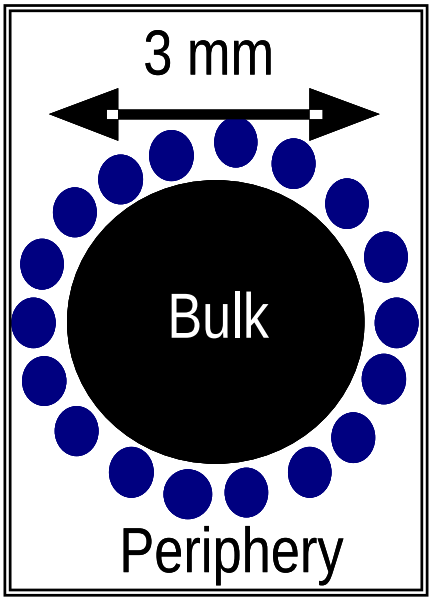

Figure 1.1 Schematic view of the sample spot on the MALDI target plate.

Supporting information 2

PSD mode spectra of some peaks

(1)

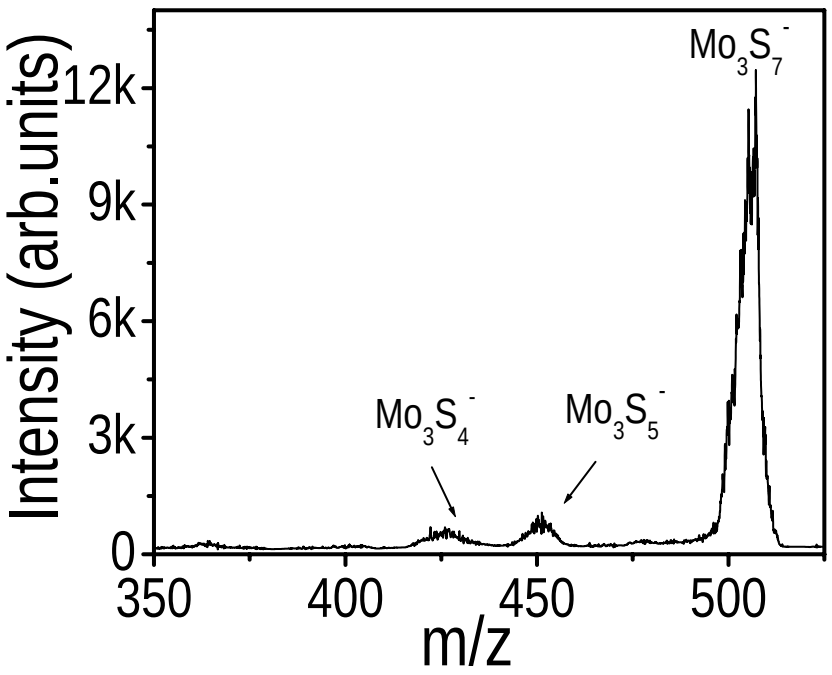

Figure 2.1. PSD spectrum of $Mo_3S_7^-$ (m/z=513) showing the fragments at $Mo_3S_4^-$ (m/z=417) and $Mo_3S_5^-$ (m/z=449).

(2)

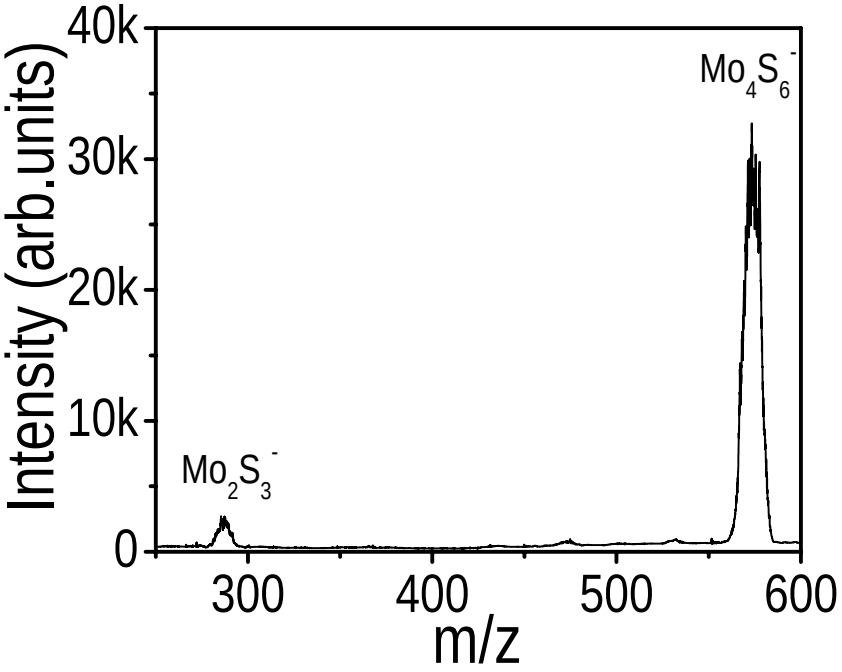

Figure 2.2. PSD spectrum of $Mo_4S_6^-$ (m/z=574) showing fragment at $Mo_2S_3^-$ (m/z=285).

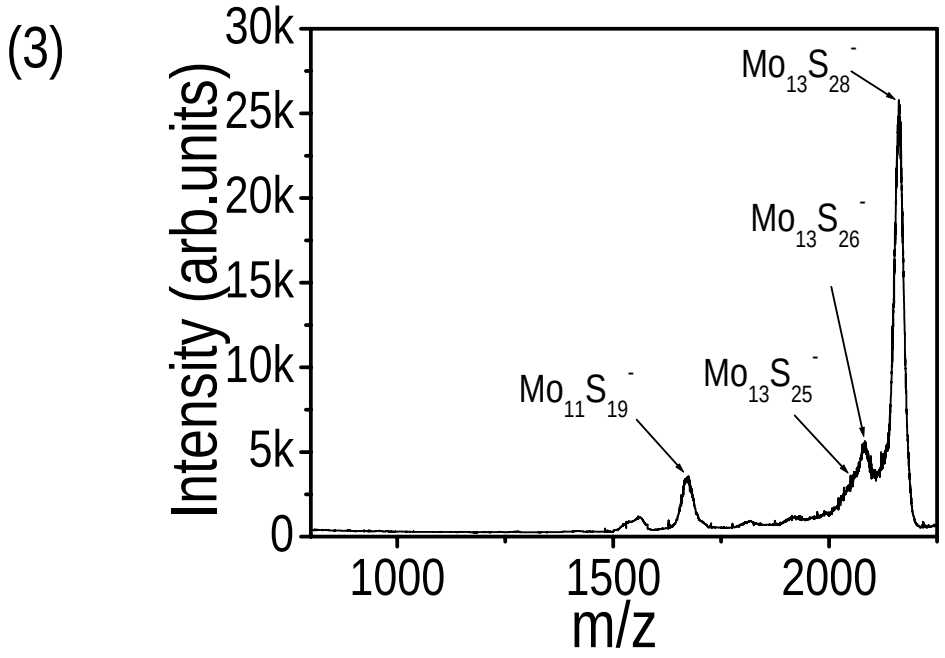

Figure 2.3. PSD spectrum of $Mo_{13}S_{28}^-$ showing the fragment ions, $Mo_{13}S_{26}^-$ (m/z 2081), $Mo_{13}S_{25}^-$ (m/z 2049) and $Mo_{11}S_{19}^-$ (m/z 1664).

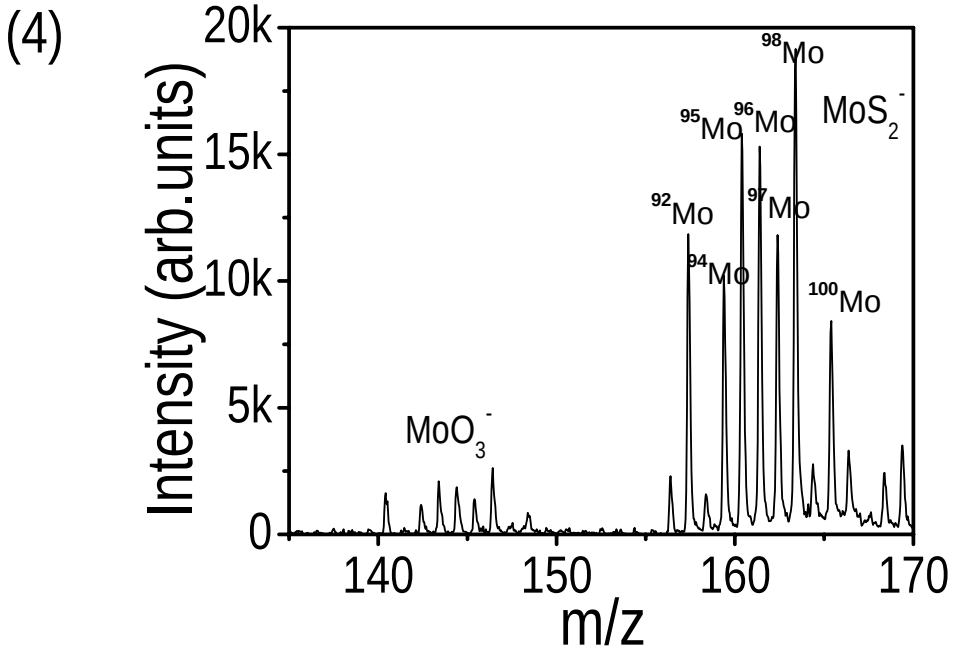

Figure 2.4. Spectrum showing peaks due to MoO_3 and MoS_2 with clear isotope resolution.

Supporting information 3

Various analyses in the extracted MoS_2 flakes.

(1)

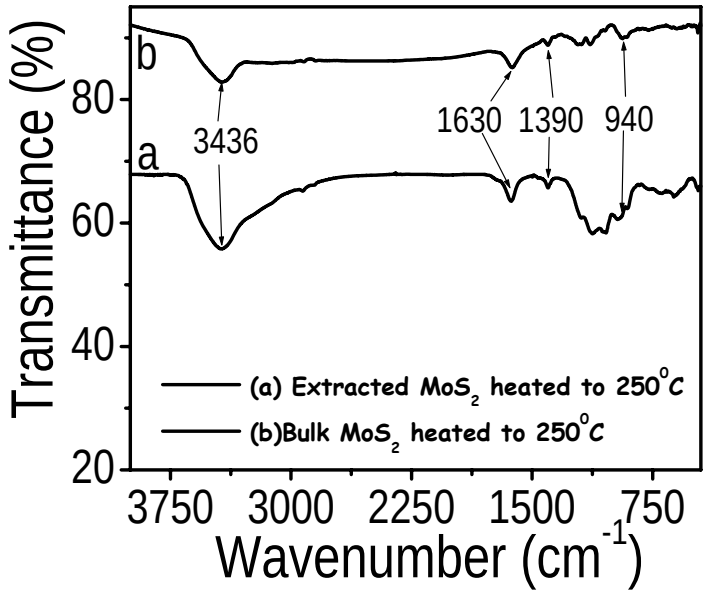

Figure 3.1. The infrared spectrum of the MoS_2 extract (a) is compared with bulk MoS_2 (b). There is a one to one correspondence between the peaks. Minor changes are attributed to the particle size effects (Maugea, F.; Lamotte, J.; Nesterenko, N. S.; Manoilova, O.; Tsyganenko, A. A.; *Catalysis Today* 2001, 70, 271–284).

(2)

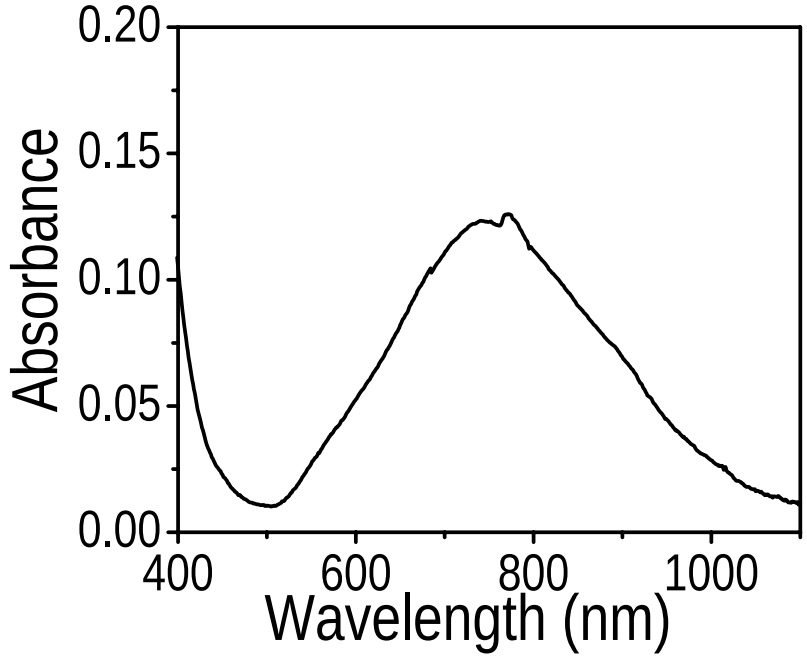

Figure 3.2. UV-Visible spectrum of extracted MoS_2 nano flakes. The peak maximum is at 770 nm.

(3)

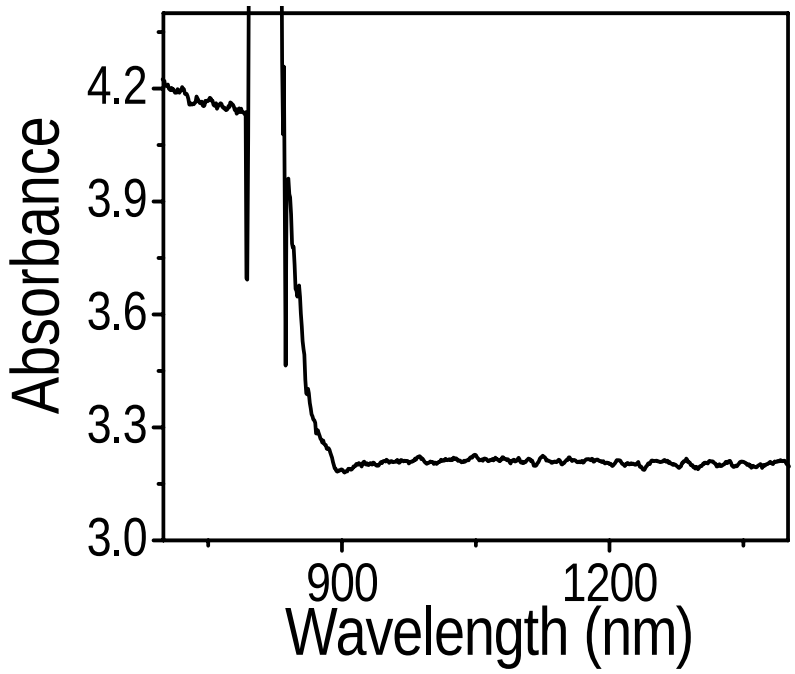

Figure 3.3. UV-Visible diffused reflectance spectrum of bulk MoS_2 showing the bulk band gap of 1.37 eV (Mattheiss, L. F.; *Phys. Rev. Lett*., 1973, 30, 784-787). The spike around 850 nm is due to a change in the light source of the instrument.

(4)

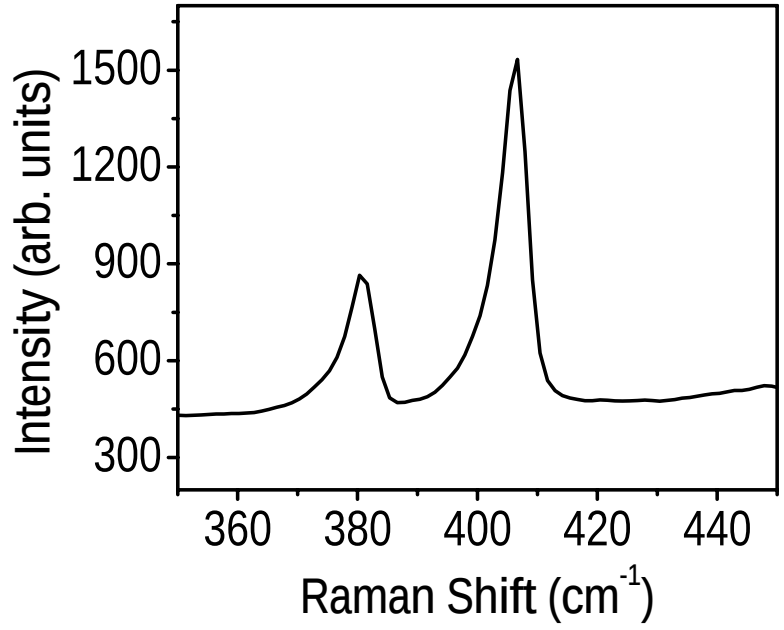

Figure 3.4 Raman spectrum of MoS_2 nanoflakes with 514 nm excitation. The spectrum was measured with a Witec confocal Raman microscope.

Supporting information 4

Spectra in ion selection mode

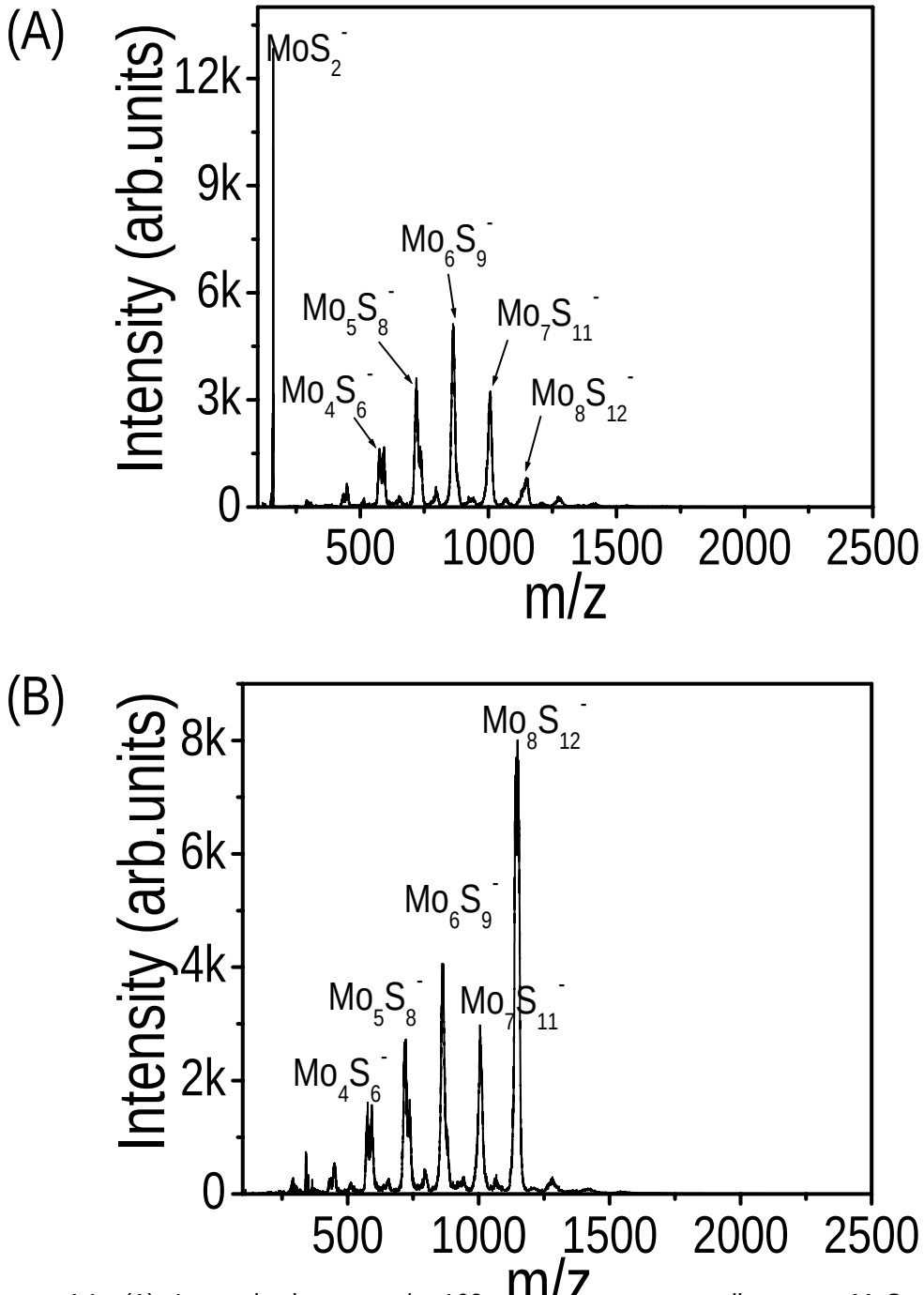

Figure 4.1. (A) Ion selection at m/z 162 corresponding to MoS_2^-, (B) ion selection at m/z 1146 corresponding to $Mo_8S_{12}^-$. While the first one shows extensive clustering, the other shows regular fragmentation. In both Mo_{13} peak was not present.

Supporting information 5

(1)

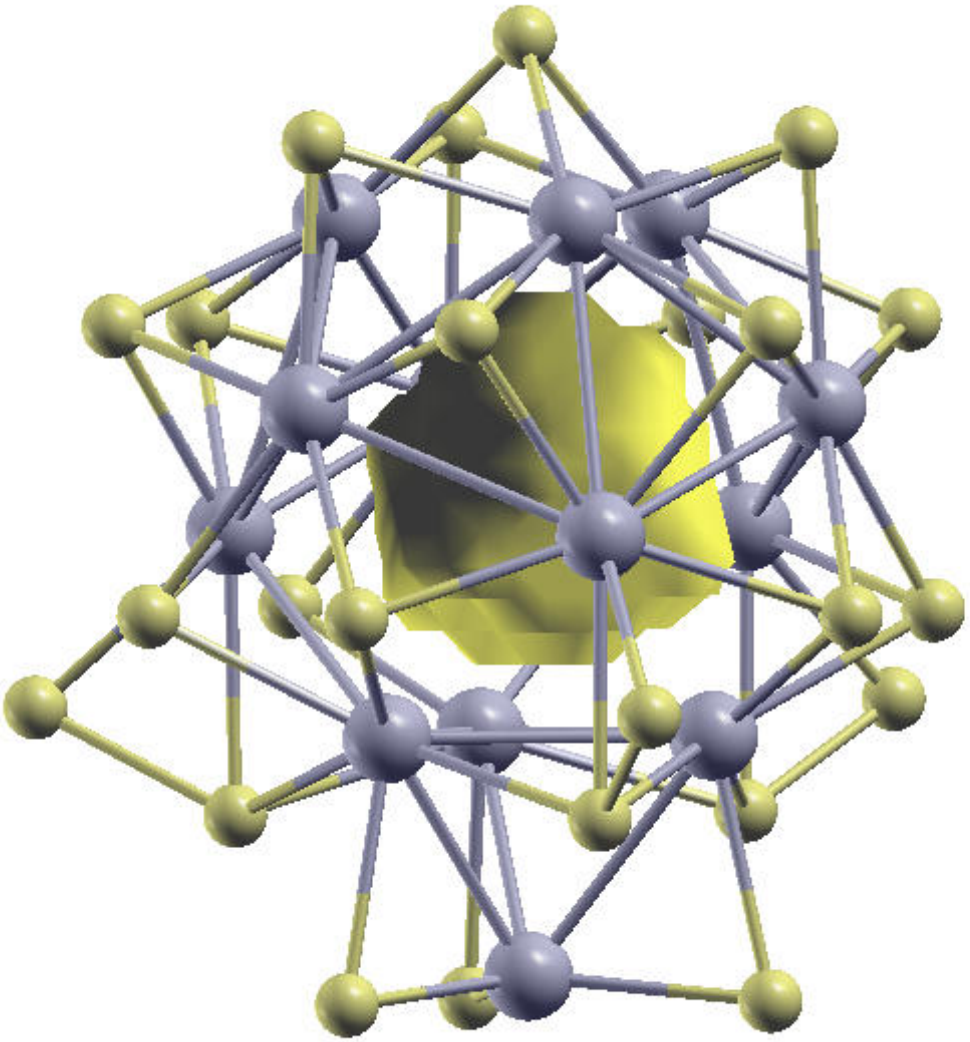

Figure 5.1. Atomic structure of the $Mo_{13}S_{25}$ cluster. A cloud in the center is plotted as a complement of charge density (region where the density is very close to zero), clearly showing the void space enclosed inside the cage-like structure of the $Mo_{13}S_{25}$ cluster.

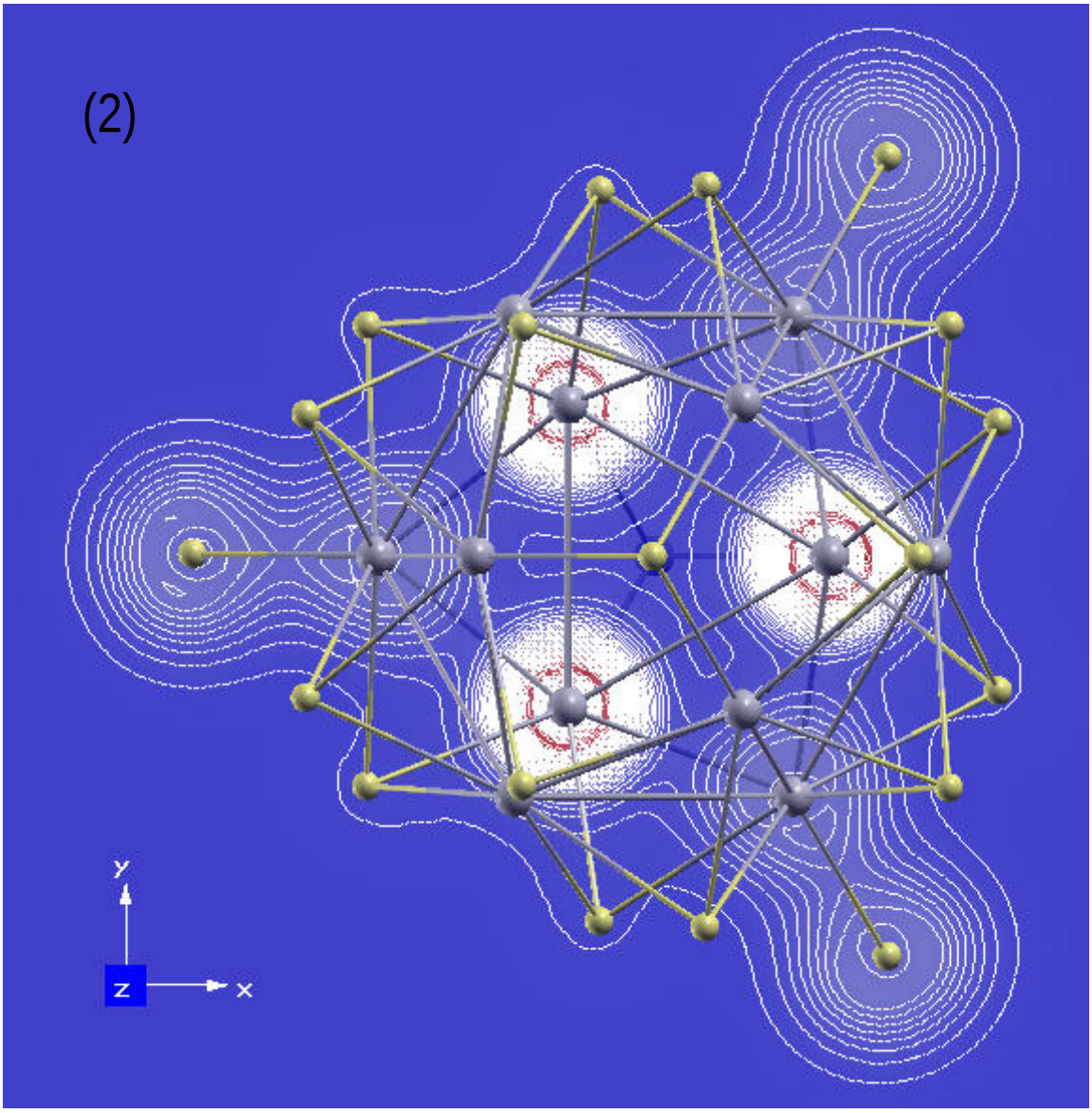

Figure 5.2. Charge density contours of the $Mo_{13}S_{25}$ cluster, viewed along z-axis (top view of the structure in Figure 1). Plane of the contours is chosen near the bottom triangle of Mo atoms such that it passes through both Mo-S and S-S bonds. Red and White colored rings centered on Mo atoms correspond to fully occupied semi-core 4s and 4p states. Angular contours near the Mo-S bonds indicate their mixed ionic and directional covalent character.

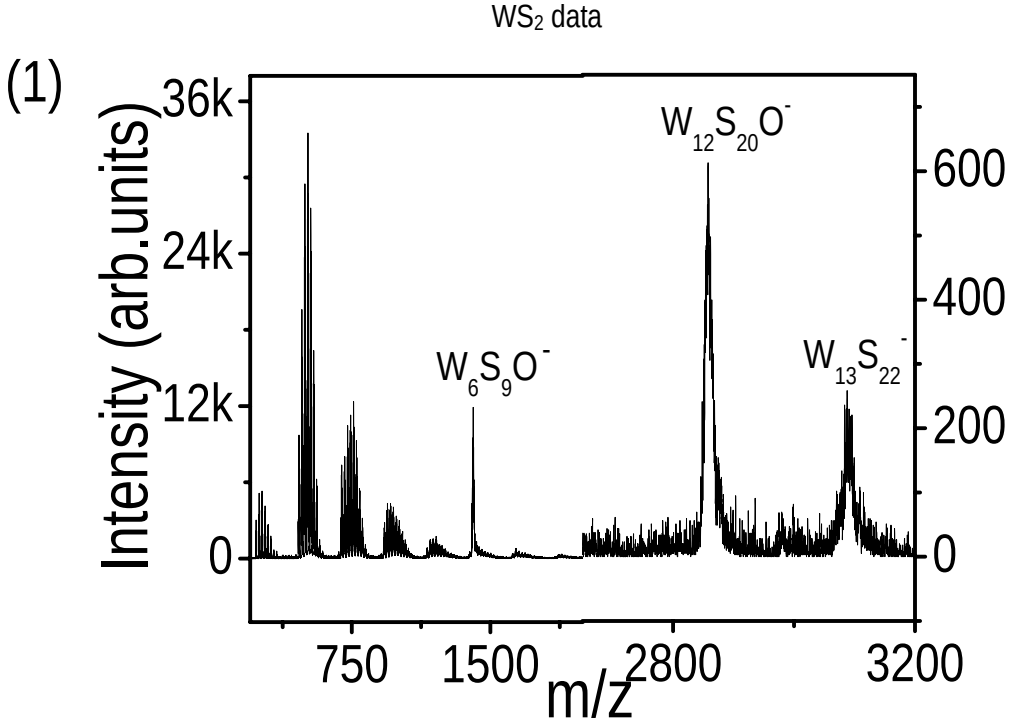

Figure 6.1. LDI spectrum of WS_2 showing magic clusters around the W_6 cluster. The W_{12} and W_{13} clusters are zoomed.

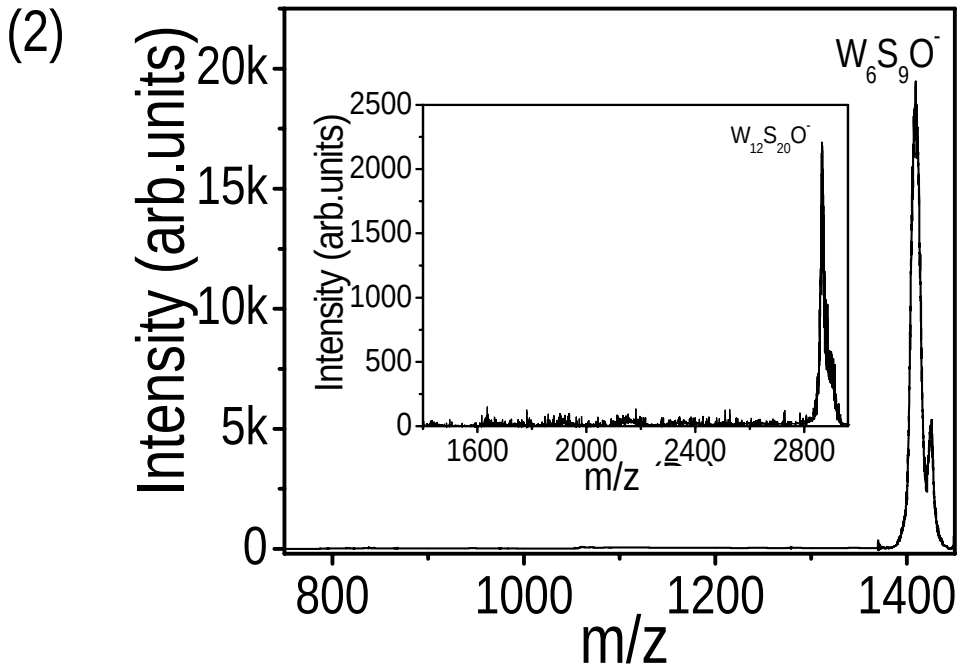

Figure 6.2. PSD mode LDI mass spectrum of $W_6S_9O^-$ showing no fragmentation. Inset: PSD of $W_{12}S_{20}O^-$ showing no fragmentation.