Reconstruction of the real distribution of the relative yields of the clusters of polyisotopic elements sputtered from MoS_2 under laser desorption/ionization

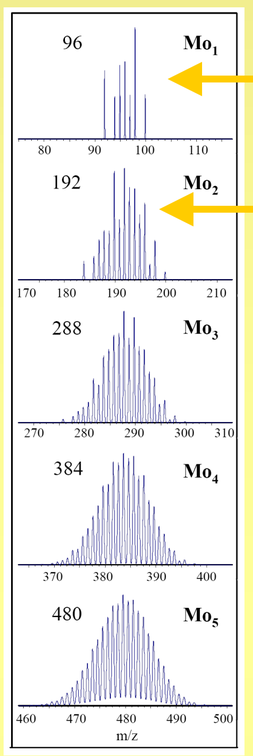
V.V. Orlov[1], O.A. Boryak[1], V.S. Shelkovsky[1], M.V. Kosevich[1], P.O. Kuzema[2]

[1] B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine, 47, Nauky Ave., 61103, Kharkiv, Ukraine, e-mail: mvkosevich@gmail.com

[2] Chuiko Institute of Surface Chemistry of the National Academy of Sciences of Ukraine, 17, Oleh Mudrak Str., 03164, Kyiv, Ukraine, e-mail: coralchance@gmail.com

Desorption/Ionization Mass Spectra of nonmolecular inorganic solids have some specific features:
- the material is sputtered in the form of clusters;
- polyisotopic chemical elements are recorded as a "peaks envelope" with appropriate isotopic distribution.
OBJECT: Molybdenum Disulfide MoS_2 and its Laser Desorption/Ionization (LDI) mass spectra.

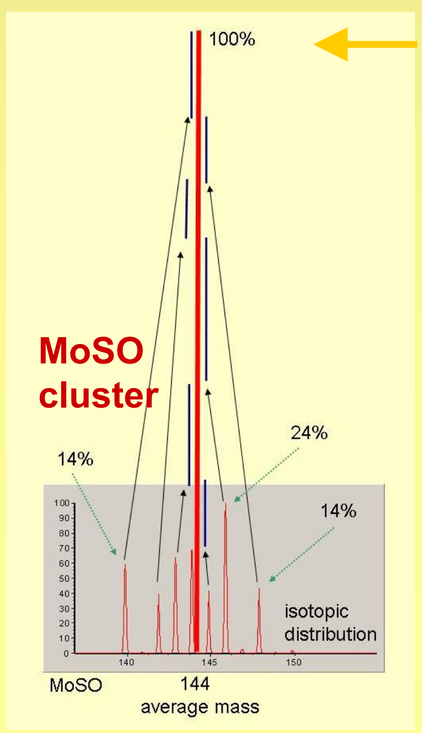
In cluster science, mass spectrometry is an efficient tool that permits the simultaneous generation and study of small atomic and molecular clusters. As a rule, the relative yield of a cluster Mn to the total population monotonically decreases with increasing n for a monocomponent object. However, the situation may be different for multicomponent objects, where cluster assembly is governed by intermolecular interactions of varying strengths among different components. This is the case of clusters sputtering from oxidized transition metal dichalcogenides, MoS_2 in particular. The pattern of $Mo_xS_yO_z^-$ clusters sputtered under LDI mass spectrometric conditions from MoS_2 consists of several groups of clusters formed due to the assembly of chalcogens (S, O) around molybdenum atoms (x = 1-4).



Molybdenum is a polyisotopic element. It is represented in nature by 7 stable isotopes recorded in the mass spectra at 92, 94, 95, 96, 97, 98, 100 u. The larger the cluster Mo_n, the wider its isotopic distribution.

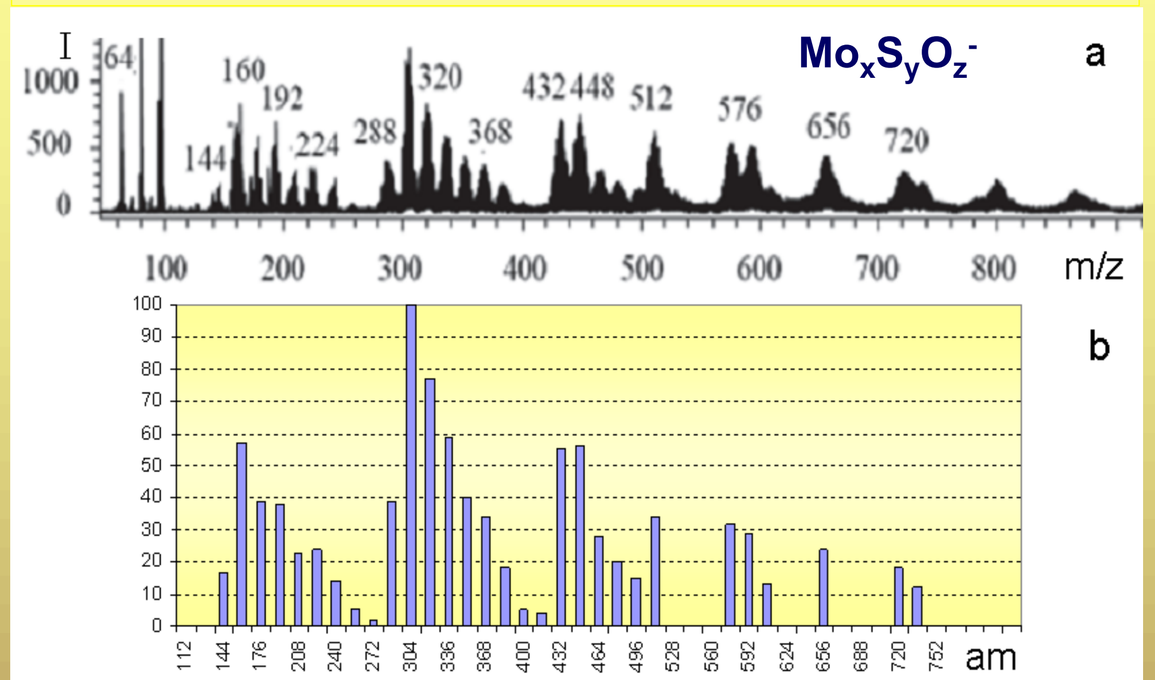
Cluster Mo_n	mass range, u., integer value	number of peaks	average mass, u., integer value	max peak % of 100%
Mo_1	92 - 100	7	96	24%
Mo_2	184 – 200	15	192	13%
Mo_3	276 – 300	23	288	11%
Mo_4	368 - 400	31	384	8%
Mo_5	460 - 500	39	480	7%

We proposed to describe the position of a cluster in the mass spectrum by the calculated average mass of its isotopic distribution [1].



The 100% of a cluster content is distributed over the related isotopic distribution, that is, the set of peaks in the mass spectrum.
As a consequence, the intensity of the maximal peak in the set decreases with *n* increase in relation to the total 100%.
The AIM of this work was to "reconstruct" the real contributions of $Mo_xS_yO_z^-$ clusters sputtered under LDI from MoS_2 by recalculating the value of 100% abundance of isotopic distributions for each cluster in the spectrum.

Original negative ion LDI mass spectrum of MoS_2 (a).
It contains sets of clusters $Mo_xS_yO_z^-$



[1]. Boryak O.A., Kosevich M.V., Pashynska V.A., Kuzema P.O., Karachevtsev V.A. On laser desorption/ionization mass spectrometry of molybdenum disulfide 2D nanomaterial // Chemistry, Physics and Technology of Surface, 2025, 16 (2), 178-190.

A computer program was written to compare the calculated isotopic distributions with ion abundance data derived from the original mass spectra.
The results of the reconstruction are presented as a histogram, in which the calculated abundances are plotted versus the average mass values of the clusters. It can be seen that the total pattern of the two clusters' distributions is similar, while the maximum intensities in the experimental envelopes of peaks for larger clusters are lower than the calculated ones.
The visual difference appeared to be not as large as it was expected.

Additional comments. When this work was completed, a more thorough analysis of clusters revealed that some clusters are superpositions of several similar structures, which will be described in our poster "Modification of transition metal dichalcogenides by organic compounds, reflected in the composition of laser-desorbed clusters". This finding underscores the need to separate the contributions of these structures in subsequent calculations.

CONCLUSION: The "restoration" of the 100% yield of polyisotopic clusters revealed relatively small difference between the calculated and experimental abundances.

EXPERIMENTAL Exfoliated MoS_2 was prepared in aqueous medium using piezoelectric oscillator generating 1700 kHz frequency. LDI mass spectrometric experiments were performed with MALDI-TOF Autoflex II LRF20 instrument (Bruker Daltonics, Germany) applying UV laser operating at 337 nm.

Acknowledgements. This work was supported by the NAS of Ukraine grant 0126U001857