

On the formation of multiple Mo–Mo bonded units in highly viscous matrix of declustered ions

BORIS UDOVIC

Faculty of Chemistry and Chemical Technology, University of Ljubljana,
Aškerčeva 5, Box 537, 1001 Ljubljana, Slovenia

MS received 7 September 1998

Abstract. Theoretically predicted but experimentally always elusive Mo_2^+ dimers were sputtered by FAB Cs^+ beam from a highly electrostricted ionic matrix and observed in its free form. Concentrated solutions of electrolysed MoO_3 trioxide in aqueous hydrochloric acid constitute a useful source, of not particularly stable, $\text{Mo}_2\text{Cl}_9^{3-}$ ions. Caged $\text{Mo}_2\text{Cl}_9^{3-}$ species in glassy viscous hydrochloride solutions were declustered within a temperature spike over 3000 K by fast atom impacts from surrounding matrix phase explosion beyond the spinodal line. Numerically precomputed m/z mass spectra collimate with observed and highly resolved lines in natural isotopic distribution amplitudes of survived Mo_2^+ species.

Keywords. Dimolybdenum molecule; FAB spectra; molybdenum dimerization; sextuple bond.

1. Introduction

Flash photolysis¹ of gaseous molybdenum hexacarbonyl $\text{Mo}(\text{CO})_6$, pulsed laser vaporization within pulsed supersonic nozzles² or high temperature effusates of very refractory bulk metals from Knudsen cells³ constitute the classic approach to gas phase observations of free molecular Mo_2 dimers by spectrographic and mass spectrometric methods. Cryochemical synthesis⁴ with condensation or co-condensation of hot metal atoms into ultracold clusters, irreversibly trapped in various noble gas matrices⁵, are the main pathway of IR-UV-VIS spectroscopic investigations⁶ on the nature and origins of the sextuple bond⁷ in Mo_2 molecules. However, the previously reported gas phase dimerization equilibrium $2\text{Mo}(\text{g}) = \text{Mo}_2(\text{g})$ preclude the synthesis of larger samples of Mo_2^{n+} species.

The alternative synthesis^{8–9} of Mo_2^{n+} dimers start from electrolysed hydrochloric solutions of MoO_3 trioxide and involve dimerization reactions of reduced molybdenum(III) complex species by progressive concentration of matrix solutions. In the present research; the high temperature declustering processes on preformed and solvated $\text{Mo}_2\text{Cl}_9^{3-}$ anions open a new pathway to obtain the free Mo_2^+ entity which survives from the extreme conditions of a “*phase explosion*” environment.

2. Experimental

Dark red solutions of molybdenum(III) complex ionic species were obtained by cathodic electroreduction of molybdenum(VI) oxide (14.4 g MoO_3 dissolved in 100 ml 36.2% HCl, sp. gr. 1.18) on Pb/Hg thin film electroactive surface. Each electrolysed

sample was concentrated by evaporation on high vacuum line from its original volume V_0 to a set of volumes: $1/2 V_0$, $1/4 V_0$, $1/8 V_0$ and $1/16 V_0$. Few drops of the above liquid samples were loaded onto the target support of a UHV ($\leq 10^{-4}$ Pa) inlet chamber equipped with a 25 KV caesium positive-ion gun. Positive and negative ionic species were sputtered from viscous matrix solutions by Fast Atom Bombardment (FAB) and analysed on AutoSpecEQ (Micromass, Manchester UK) high resolution mass spectrometer. The accelerating voltage was 8 KV. However, the most prominent m/z peaks of positive and negative ions appeared almost ~ 15 min after any liquid drop dried to a glassy viscous matrix. All sampled solutions produced mass spectra of nearly the same kind, independent of the starting concentrations.

3. Results and discussion

The first attempts of the present work involved the synthesis of $\text{Mo}_2\text{Cl}_9^{3-}$ anions in aqueous solutions of highly concentrated molybdenum(III) species. The glassy viscous matrix on the target support produced mass spectra of the type recorded in figure 1. All m/z peaks are composite and appear in accordance with the natural isotopic distribution amplitudes of the molybdenum element. Therefore, the observed peaks were assigned to different binuclear molybdenum(III) complexes. The emerging amplitudes of observed $(m/z 295)\text{Mo}_2\text{Cl}_3^{1-}$, $(m/z 332)\text{Mo}_2\text{Cl}_4^{1-}$, $(m/z 371)\text{Mo}_2\text{Cl}_5^{1-}$ and $(m/z 405)\text{Mo}_2\text{Cl}_6^{1-}$ centroids together with clear signals of some larger polynuclear clusters $(m/z 463)\text{Mo}_4\text{Cl}_2^{1-}$, $(m/z 500)\text{Mo}_4\text{Cl}_3^{1-}$ and $(m/z 534)\text{Mo}_4\text{Cl}_4^{1-}$ visibly grew

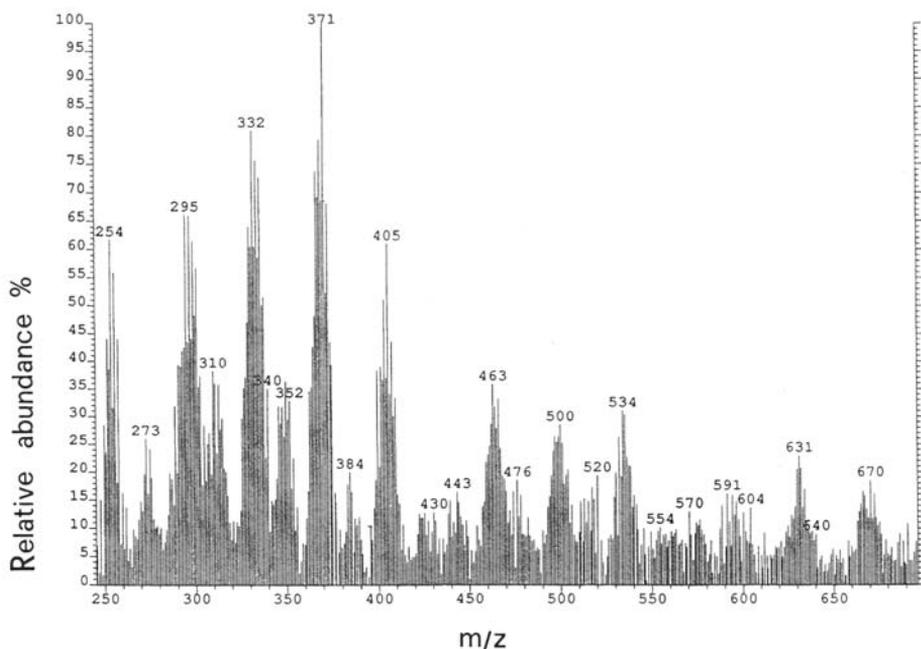
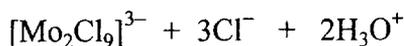
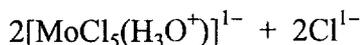
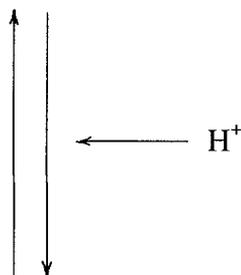
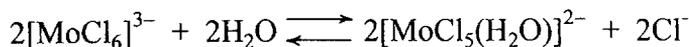


Figure 1. Partial negative-ion FAB Cs^+ mass spectrum ($250 \leq m/z \leq 690$) of binuclear and polynuclear molybdenum(III) complexes from a glassy viscous hydrochloric matrix. The scan was obtained 15 min after introduction of the sample drops into the ion beam.

up after the target samples were dehydrated by prolonged evaporation in the UHV inlet chamber. The $(m/z \sim 35\text{-}45)\text{Cl}$ shift appears to be a constant which separates the profiled peaks of the above identified clusters.

Scheme 1 and figure 2 resume the pre-supposed dimerization equilibria of monomeric MoCl_6^{3-} species investigated in this research. Captured protons by coordinated water molecules produce hydrated species H_3O^+ , which immediately leave from their coordination sites. An analogous detachment of coordinated chloride anions Cl^- as contact ion-pairs $\text{Cl}^- \text{H}^+$ or molecular HCl leaving groups constitute a less violent and comparatively, a less frequent event. However, both the above declustering processes can shift the dimerization equilibria towards the binuclear $\text{Mo}_2\text{Cl}_9^{3-}$ complex formation and allow an irreversible removal of gaseous H_2O and HCl components during the high vacuum evaporation process. Beside this, equilibrated solvolytic reactions on MoCl_6^{3-} species produce some aquated mononuclear complexes which are the presupposed precursors of $\text{Mo}_2\text{Cl}_9^{3-}$ dimers. The opposite electrostatic charges in mononuclear species MoCl_5 are algebraically balanced and a dimerization reaction between uncharged groups is less hindered in comparison with long range repulsions between highly charged anions MoCl_6^{3-} . In dilute electrolytic solutions, the unbalanced repulsive charges within $\text{Mo}_2\text{Cl}_9^{3-}$ promote the disintegration of their binuclear core. On the other hand, in the glassy viscous hydrochloric matrix, the field of free contacting protons shield and minimize the effective charge on coordinated ligands. Therefore, the labilizing power of repulsing charges from distal positions is less prominent and the existence of $\text{Mo}_2\text{Cl}_9^{3-}$ anions is favoured. Some smaller, but more mobile monodentate ligands as H_2O or Cl^- , quickly and



Scheme 1. The solvolytic and dimerization reaction equilibria of molybdenum(III) complexes within concentrated hydrochloric solutions.

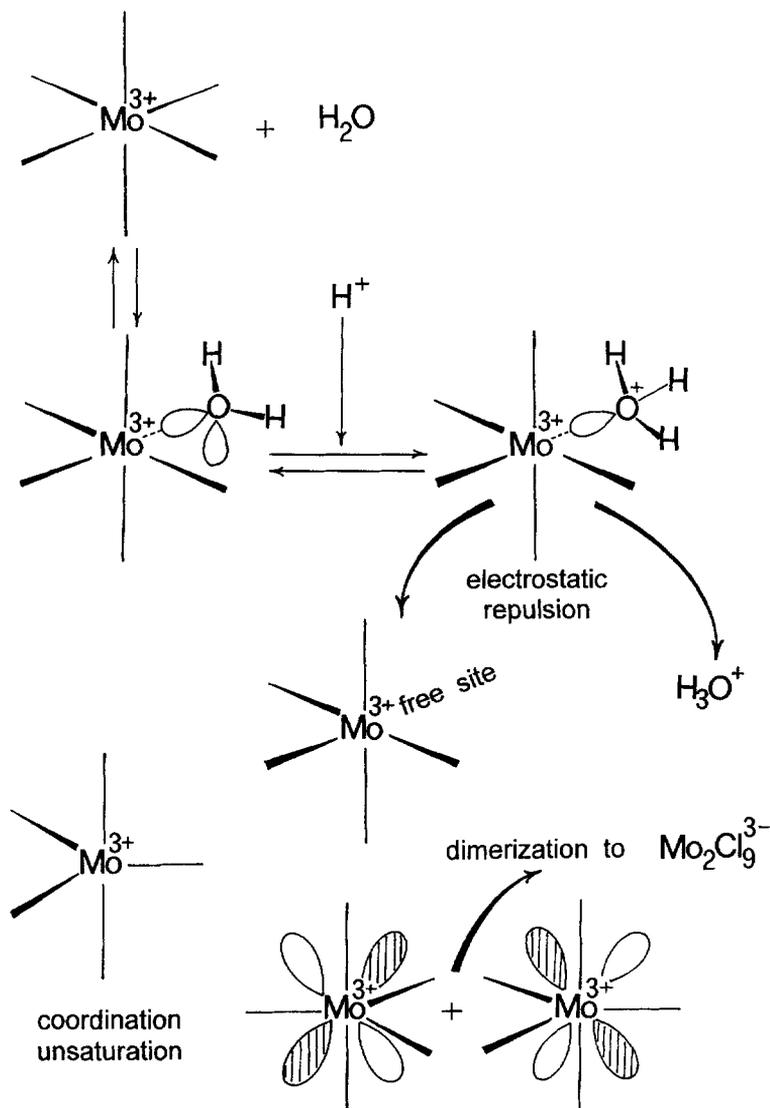


Figure 2. Possible intermediates and dimerization reactions with declustered molybdenum(III) ionic species in a highly viscous hydrochloric matrix.

competitively modify the coordination inner sphere of monomeric cations Mo^{3+} by solvolytic and anation reactions, as a result of which the dimerization processes in diluted solutions are unfavoured. Some peaks shown in figure 3 were assigned to the most probable species: $(m/z\ 203)\text{MoCl}_3^{-}$, $(m/z\ 219)\text{MoCl}_3^{-}(\text{H}_2\text{O})$, $(m/z\ 236)\text{MoCl}_3^{-}\cdot 2(\text{H}_2\text{O})$, $(m/z\ 254)\text{MoCl}_3^{-}\cdot 3(\text{H}_2\text{O})$. The $(m/z \sim 18\ \text{H}_2\text{O})$ shift between the above centroids suggest the presence of various aquated complexes. However the existence of MoCl_6^{3-} and $[\text{MoCl}_5(\text{H}_2\text{O})]^{2-}$ anions within electrolysed hydrochloric solutions of the starting compound MoO_3 is well established⁸⁻⁹. On the other hand, the thermal motions of charged particles in a highly viscous matrix are characterized by

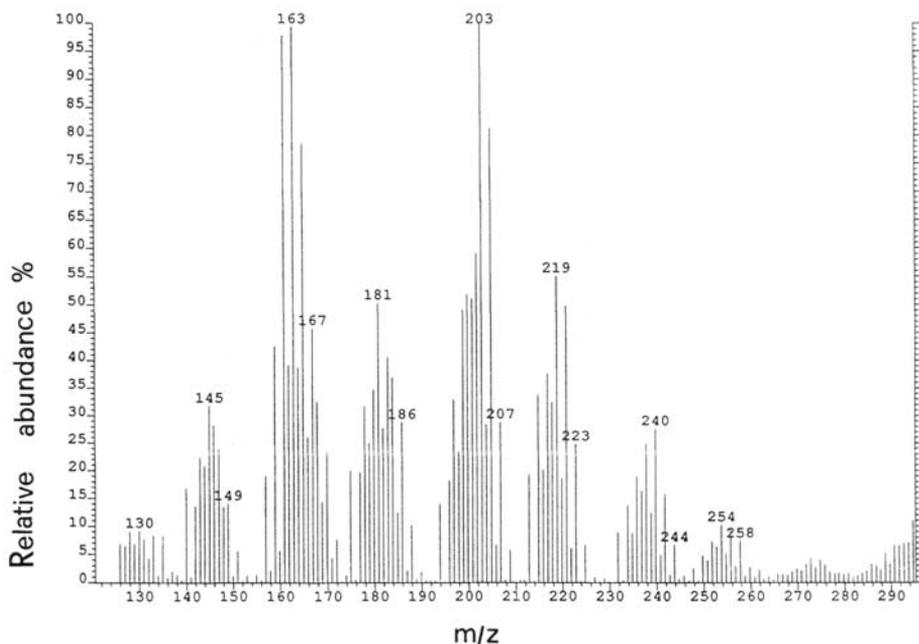


Figure 3. Partial negative-ion FAB Cs^+ mass spectrum ($120 \leq m/z \leq 290$) of mononuclear molybdenum(III) complexes from a glassy viscous hydrochloric matrix. The scan was obtained 15 min after introduction of the sample drops into the ion beam.

low values of their microscopic translational mobility and by remarkably shorter diffusion shifts. Therefore, the inner-sphere leaving groups are readily and irreversibly trapped by the surrounding ionic atmosphere. The hydrated protons H_3O^+ capture some water molecules, whose dipoles are oriented in the field of the ion, and build up H_9O_4^+ or higher species by a network of hydrogen bonds^{10–12}. The resulting hydrogen-bonded ice-like clusters of water molecules have a prevailing open structure and increase the growth of the macroscopic viscosity. In the glassy matrix the reactive species can travel only through very short distances. The correlation between reactivity and frequency of thermal collisions among particles of comparable sizes is suggested by the simple Einstein-Stokes diffusion model in which the diffusion coefficient is inversely proportional to the cuberoot of the molar mass M

$$D = RT/N_A 6\pi\eta \left(\frac{4\pi N_A}{3Mv} \right)^{1/3}$$

where N_A is the Avogadro constant, v is the specific volume of a particle and η is the macroscopic viscosity of the liquid matrix.

However, due to the exponential dependence of the viscosity η on T , the solvolytic and anation reactions are highly affected by diffusion phenomena. If an inner sphere group (lower M , higher D) is far apart from its substrate, the coordination number of Mo(III) ions decreases and the coordination unsaturation becomes more and more common. Therefore the reactive collisions between neutral and neighbouring complex halides (higher M , lower D), as idealized in figure 2 is more favoured. Some

multiple σ_z , π_x , and π_y bonds link together the monomeric molybdenum(III) complex halides along their collision line axis and originate some binuclear species in tervalent state.

The highest m/z peaks of binuclear complex anions were detected 15 min after the sample drops had evaporated. Therefore a very low concentration of cluster species was supposed to exist at the top surface of the solution matrix. The mononuclear and binuclear molybdenum(III) complexes with free protons as counter-ions are of a highly hydrophilic species, and they therefore exhibit some reluctance to exist at vacuum-water interface. Moreover the UHV speedy evaporation of water molecules and other volatile components from the target, drops, immediately cools down and the original matrix stratifies into an epilayer of ice and a liquid underlayer of hydrated species. As soon as the glassy viscous matrix is formed, the hydrated electrolytes can emerge from the innermost layers. The fast impacting 25 KV Cs^+ beam releases a lot of kinetic energy in a very small volume of the sample surface by direct momentum transfer to the surroundings from recoiling atoms in the primary collision cascade¹³. A violent transition from the superheated and metastable liquid-phase to a dense gas-like state is performed at over 3000 K. A qualitative explanation on the observed extent of clustering and declustering phenomena is given by the localized "Phase Explosion" model¹⁴, where the liquidus surface of a liquid-phase diagram is considered beyond the stable liquid-vapour equilibrium curve. The high heating rates press the liquid to overshoot the limit of superheat absolute instability, i.e. the spinodal line which connects minima in extrapolated metastable liquid and maxima in extrapolated metastable gas. Beyond the spinodal, the pressure increases as the volume increases (at constant temperature). A single particle is then rapidly thermalized and cooled down to low temperatures during the fast expansion following a phase explosion. In this work, the matrix-derived ions produced by collision cascades perform the most important declustering processes on binuclear ions as $\text{Mo}_2\text{Cl}_9^{3-}$. However the concept of liquid secondary ionization mass spectrometry (SIMS)¹⁵ appears to be a more correct term to correlate some observed facts and evidences. High temperature derived particles strike the outermost electrons of de-absorbed binuclear molybdenum(III) complexes and cause the immediate expulsion of ligands from their coordination site. The declustering processes in a system with a large number of dimolybdate(III,III) anions are more frequent and more probable in comparison with high temperature reactive collisions between isolated and diluted Mo^{n+} bare ions. Therefore the declustered $\text{Mo}_2\text{Cl}_9^{3-}$ ions seem to be a reasonable source of expected free dimers Mo_2^+ . The mass spectrum recorded in figure 4 include some relevant peaks (m/z 184), (m/z 186), (m/z 187), (m/z 188), (m/z 189), (m/z 190), (m/z 191), (m/z 192), (m/z 193), (m/z 194), (m/z 195), (m/z 196), (m/z 197), (m/z 198) and (m/z 200), which were assigned to the natural isotopic distribution amplitudes of free Mo_2^+ ions. The precomputed spectral profile shown in figure 5 is congruent with the above isotopic distribution in the $184 \leq m/z \leq 200$ range. The violently exploding metastable phase at over 3000 K constitutes a thermodynamically unequilibrated system, which is not comparable with the previously reported³ gas phase dimerization equilibrium $2\text{Mo}(\text{g}) = \text{Mo}_2(\text{g})$ in Knudsen cells within the 2600–3000 K range. The observed molecular ion Mo_2^+ is therefore a descending entity from its precursor dimer Mo_2^{2+} , which was performed as a core of a binuclear molybdenum(III) complex anion in a viscous hydrochloric matrix. A significant centroid (m/z 227) is also observed in the mass spectrum of figure 4 at nearly 35 m/z units higher in comparison with the natural isotopic distribution

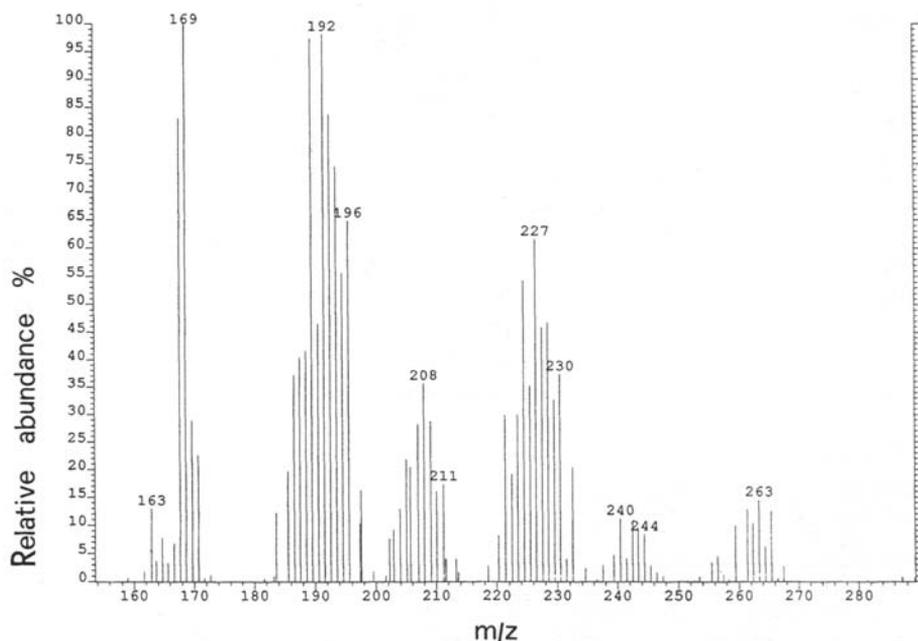


Figure 4. Partial positive-ion FAB Cs^+ mass spectrum ($160 \leq m/z \leq 280$) with visible natural isotopic distribution amplitudes of free dimers Mo_2^+ . The scan was obtained 15 min after introduction of the sample drops into the ion beam.

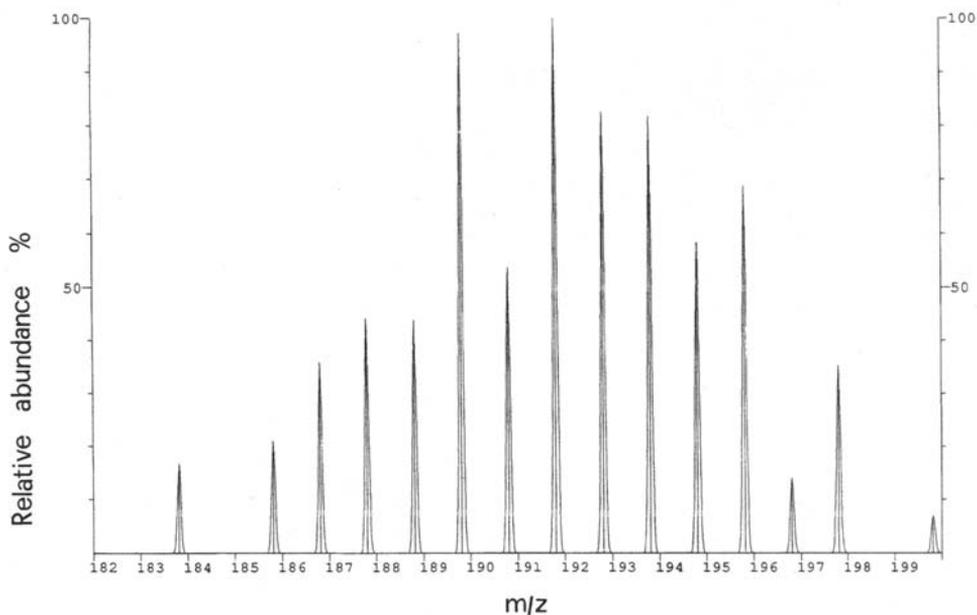


Figure 5. Calculated profile of isotope ratios for the mass spectrum of the free molecular ion Mo_2^+ .

amplitudes of Mo_2^+ . The composite signal is in reasonable agreement with the expected profile for Mo_2Cl^+ ions which are fragments of preformed clusters $\text{Mo}_2\text{Cl}_9^{3-}$.

Conclusions

A suitable source of $\text{Mo}_2\text{Cl}_9^{3-}$ dimers from inexpensive aqueous media was investigated. The existence of multiple equilibria involving mononuclear and binuclear molybdenum(III) complex halides was confirmed by FAB Cs^+ mass spectra obtained from a progressive concentration of electrolysed solutions of MoO_3 trioxide in aqueous hydrochloric matrix. The rapid reversion of $\text{Mo}_2\text{Cl}_9^{3-}$ dimers to mononuclear species arises in more diluted solutions and constitutes the key-reaction pathway which must be carefully avoided in macro-preparative syntheses.

Preformed $\text{Mo}_2\text{Cl}_9^{3-}$ dimers were declustered in high temperature processes by FAB Cs^+ impact collisions, which release the exotic Mo_2^+ entity. The observed natural isotopic distribution amplitudes in m/z mass spectra confirm the existence of survived Mo_2^+ molecular species from a thermodynamically non-equilibrated matrix kernel, flash heated over 3000 K.

References

1. Efremov Yu M, SamoiloVA A N, Kozhukhovski V B and Gurchich L V 1978 *J. Mol. Spectrosc.* **73** 430
2. Hopkins J B, Langridge-Smith P R R, Morse M D and Smalley R E 1983 *J. Chem. Phys.* **78** 1627
3. Gupta S K, Atkins R M and Gingerich K A 1978 *Inorg. Chem.* **17** 3211
4. Klotzbücher W and Ozin G A 1977 *Inorg. Chem.* **16** 984
5. Klotzbücher W, Ozin G A, Norman J G Jr. and Kolari H J 1977 *Inorg. Chem.* **16** 2871
6. Morse M D 1986 *Chem. Rev.* **86** 1049
7. Bursten B E, Cotton F A and Hall M B 1980 *J. Am. Chem. Soc.* **102** 6348
8. Hartmann H and Schmidt H J 1957 *Z. Phys. Chem.* **11** 15
9. Lewis J, Nyholm R S and Smith P W 1969 *J. Chem. Soc. (A)* 57
10. Noyes R M 1964 *J. Am. Chem. Soc.* **86** 971
11. Némethy G and Scheraga H A 1962 *J. Chem. Phys.* **36** 3382
12. Wei S, Shi Z and Castelman A W Jr. 1991 *J. Chem. Phys.* **94** 3268
13. Sunner J, Morales A and Kebarle P 1988 *Int. J. Mass Spectrom. Ion Processes* **86** 169
14. Sunner J, Ikonomou M G and Kebarle P 1988 *Int. J. Mass Spectrom. Ion Processes* **82** 221
15. Miller J M 1989 *Mass. Spec. Rev.* **9** 319