Electronic Supplementary Material (ESI) for Dalton Transactions

The formation and stability of molybdenum-antimony and tungsten-antimony ternary oxides Sb_2MO_6, $Sb_2M_2O_9$, $Sb_2Mo_3O_{12}$ and Sb_4MO_9 in the gas phase (*M* = Mo, W). Quantum chemical and mass spectrometric studies.

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Supplementary Materials

Table S1 Molecular symmetries, total energies and thermal energies of the antimony, molybdenum and tungsten oxides and their isomers (def2-TZVP/RI-BP86).

molecule	molecular symmetry	E_{tot} (a.u.)	$E_{therm\ 298}$ (kJ·mol^{-1})
Sb_4O_6 (I)	T_d	-1413.450842	84.18
Sb_4O_6 (II)	D_{2h}	-1413.408816	84.13
Mo_3O_9 (I)	C_{3v}	-882.913202	118.15
Mo_3O_9 (II)	C_{2v}	-882.874712	117.55
Mo_4O_{12} (I)	D_{4h}	-1177.237313	160.27
Mo_4O_{12} (II)	C_1	-1177.204197	159.15
Mo_5O_{15} (I)	C_s	-1471.553735	201.98
Mo_5O_{15} (II)	C_{2v}	-1471.530664	200.63
W_3O_9 (I)	D_{3h}	-879.687121	117.18
W_3O_9 (II)	C_1	-879.651945	116.62
W_4O_{12} (I)	C_{4v}	-1172.940438	159.00
W_4O_{12} (II)	C_1	-1172.914854	158.31
W_5O_{15} (I)	C_s	-1466.184910	200.43
W_5O_{15} (II)	C_{2v}	-1466.173493	199.75

Table S2 Molecular symmetries, total energies and thermal energies of the antimony, molybdenum and tungsten ternary oxides and their isomers (def2-TZVP/RI-BP86).

molecule	molecular symmetry	E_{tot} (a.u.)	$E_{therm\ 298}$ (kJ·mol^{-1})
Sb_2MoO_6 (I)	C_{2v}	-1001.015868	80.37
Sb_2MoO_6 (II)	C_s	-1000.964235	78.00
$Sb_2Mo_2O_9$ (I)	C_s	-1295.352819	122.25
$Sb_2Mo_2O_9$ (II)	C_1	-1295.331719	122.14
$Sb_2Mo_2O_9$ (III)	C_1	-1295.324831	121.21
$Sb_2Mo_2O_9$ (IV)	C_1	-1295.323287	121.18
$Sb_2Mo_2O_9$ (V)	C_1	-1295.313122	120.61
Sb_4MoO_9 (I)	C_s	-1707.773869	125.97
Sb_4MoO_9 (II)	C_4	-1707.765030	125.07
Sb_4MoO_9 (III)	C_s	-1707.753925	125.08
Sb_4MoO_9 (IV)	C_s	-1707.749597	126.03
Sb_4MoO_9 (V)	C_s	-1707.725305	126.41
Sb_4MoO_9 (VI)	C_{2v}	-1707.718893	125.12
$Sb_2Mo_3O_{12}$ (I)	C_s	-1589.671665	164.08
$Sb_2Mo_3O_{12}$ (II)	C_1	-1589.668129	164.18
$Sb_2Mo_3O_{12}$ (III)	C_1	-1589.647773	164.22
$Sb_2Mo_3O_{12}$ (IV)	C_1	-1589.637061	161.81
Sb_2WO_6 (I)	C_{2v}	-999.942317	80.01
Sb_2WO_6 (II)	C_{2v}	-999.902957	78.15
$Sb_2W_2O_9$ (I)	C_s	-1293.204927	121.50
$Sb_2W_2O_9$ (II)	C_1	-1293.186000	121.53
$Sb_2W_2O_9$ (III)	C_1	-1293.182354	120.67
$Sb_2W_2O_9$ (IV)	C_1	-1.293.186766	120.82
$Sb_2W_2O_9$ (V)	C_1	-1.293.181353	120.12
Sb_4WO_9 (I)	C_s	-1706.701626	125.62
Sb_4WO_9 (II)	C_4	-1706.705806	125.13
Sb_4WO_9 (III)	C_s	-1706.695186	125.09
Sb_4WO_9 (IV)	C_1	-1706.677443	125.75
Sb_4WO_9 (V)	C_s	-1706.653897	126.11
Sb_4WO_9 (VI)	C_{2v}	-1706.662854	125.26

Table S3 Experimental[23] and calculated thermodynamic characteristics of the molybdenum and antimony oxides (def2-TZVP/RI-BP86).

Molecule	S^0_{298} (J·mol^{-1}·K^{-1}) (exp. // QC)	S^0_{1000} (J·mol^{-1}·K^{-1}) (exp. // QC)	$c^0_{p,T} = a + b\cdot10^{-3}\cdot T + c\cdot10^{6}\cdot T^{-2}$ (exp. // QC)		
			a	*b*	*c*
Sb_4O_6	444.2 // 461.8	699.8 // 719.1	217.6 // 222.6	14.1 // 9.0	-3.5 // -3.6
Mo_3O_9	526.7 // 525.5	837.3 // 820.0	274.5 // 246.8	4.2 // 30.7	-4.8 // -5.1
Mo_4O_{12}	654.0 // 639.4	1074.2 // 1038.8	371.4 // 333.1	5.7 // 42.3	-6.5 // -6.5
Mo_5O_{15}	771.5 // 798.1	1301.3 // 1302.7	468.2 // 420.4	7.2 // 52.9	-8.2 // -8.0
W_3O_9	504.7 // 542.5	845.3 // 838.2	274.5 // 247.7	4.2 // 30.1	-4.8 // -4.9
W_4O_{12}	605.3 // 668.1	1028.9 // 1069.2	372.0 // 334.1	5.0 // 41.4	-5.9 // -6.3

Table S4 Calculated thermodynamic characteristics of the molybdenum and antimony oxides (def2-TZVP/RI-BP86).

Molecule	S^0_{298} (J·mol^{-1}·K^{-1})	$c^0_{p,T} = a + b\cdot10^{-3}\cdot T + c\cdot10^{6}\cdot T^{-2}$		
		a	*b*	*c*
Sb_2MoO_6	440.9	188.9	16.8	-3.3
$Sb_2Mo_2O_9$	566.4	273.3	31.0	-4.7
$Sb_2Mo_3O_{12}$ (I)	691.0	360.2	41.4	-6.1
$Sb_2Mo_3O_{12}$ (II)	699.9	360.3	41.4	-6.2
Sb_4MoO_9	626.3	306.6	23.0	-4.8
Sb_2WO_6	448.9	192.8	11.8	-3.5
$Sb_2W_2O_9$	593.0	281.4	20.5	-5.0
Sb_4WO_9	569.2	311.7	16.4	-5.0

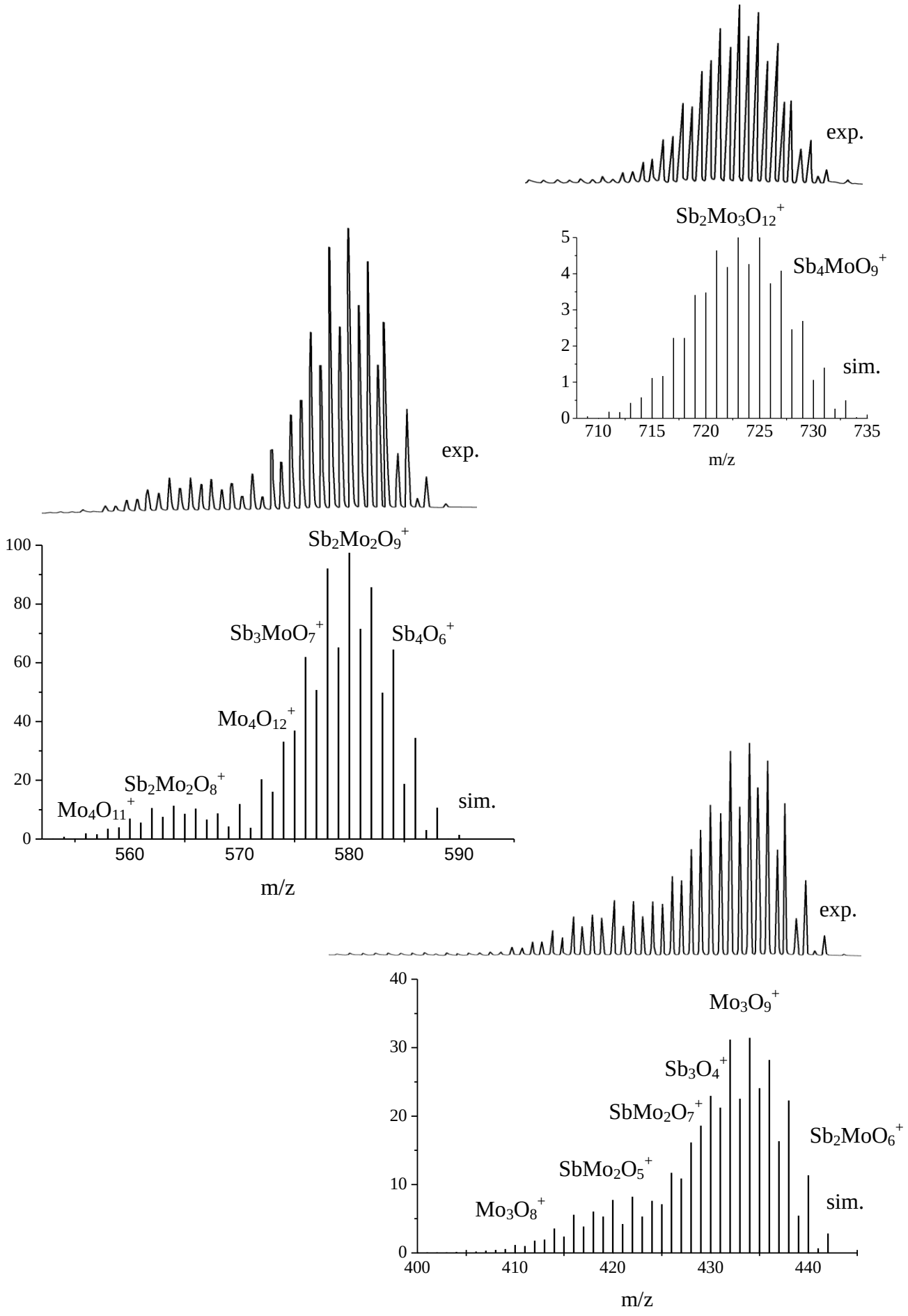

Fig. S1 Experimental and simulated mass spectra of $Sb_2Mo_3O_{12}$, 893 K, 70 eV.

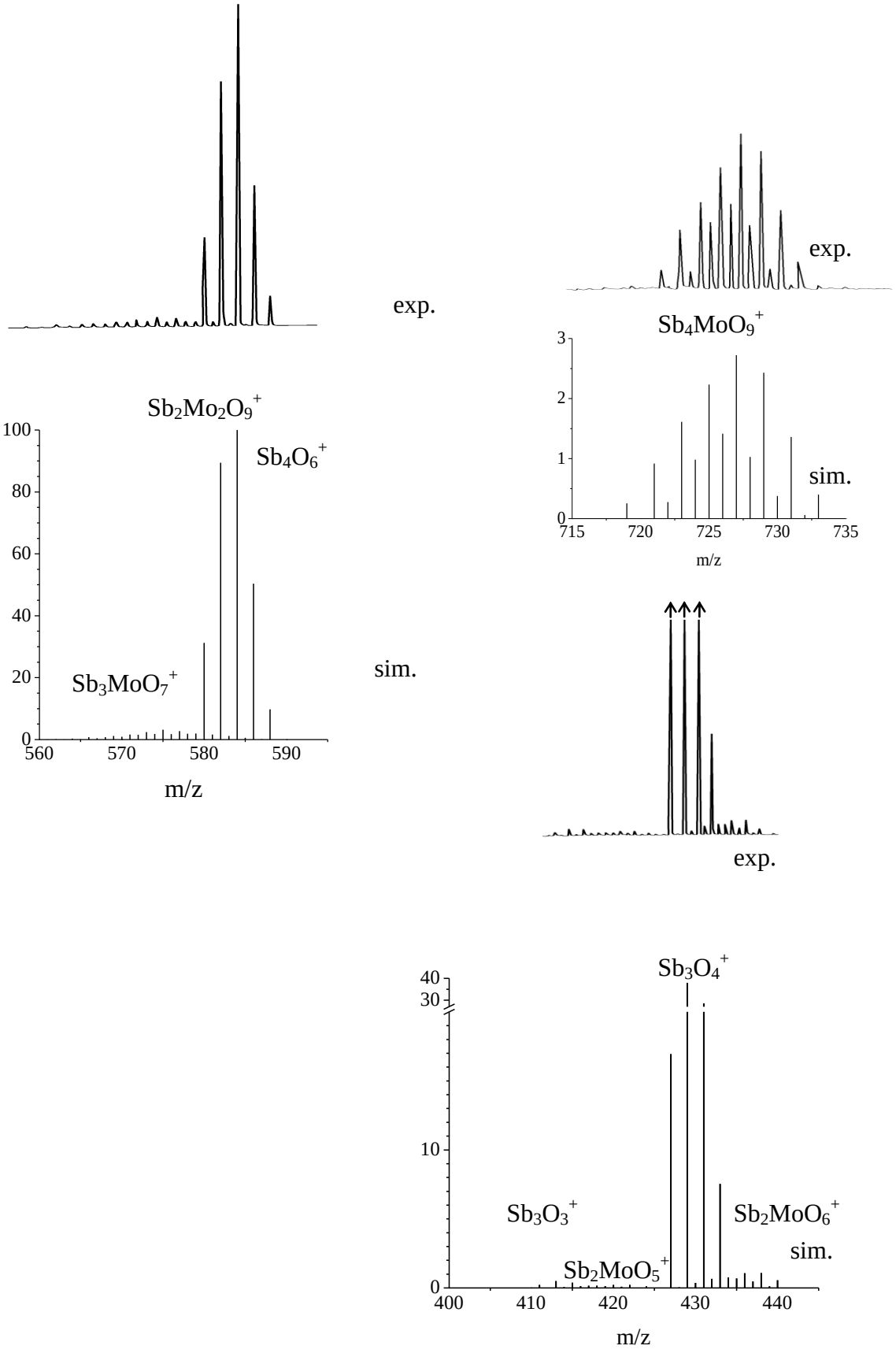

Fig. S2 Experimental and simulated mass spectra of Sb_2MoO_6, 840 K, 70 eV.

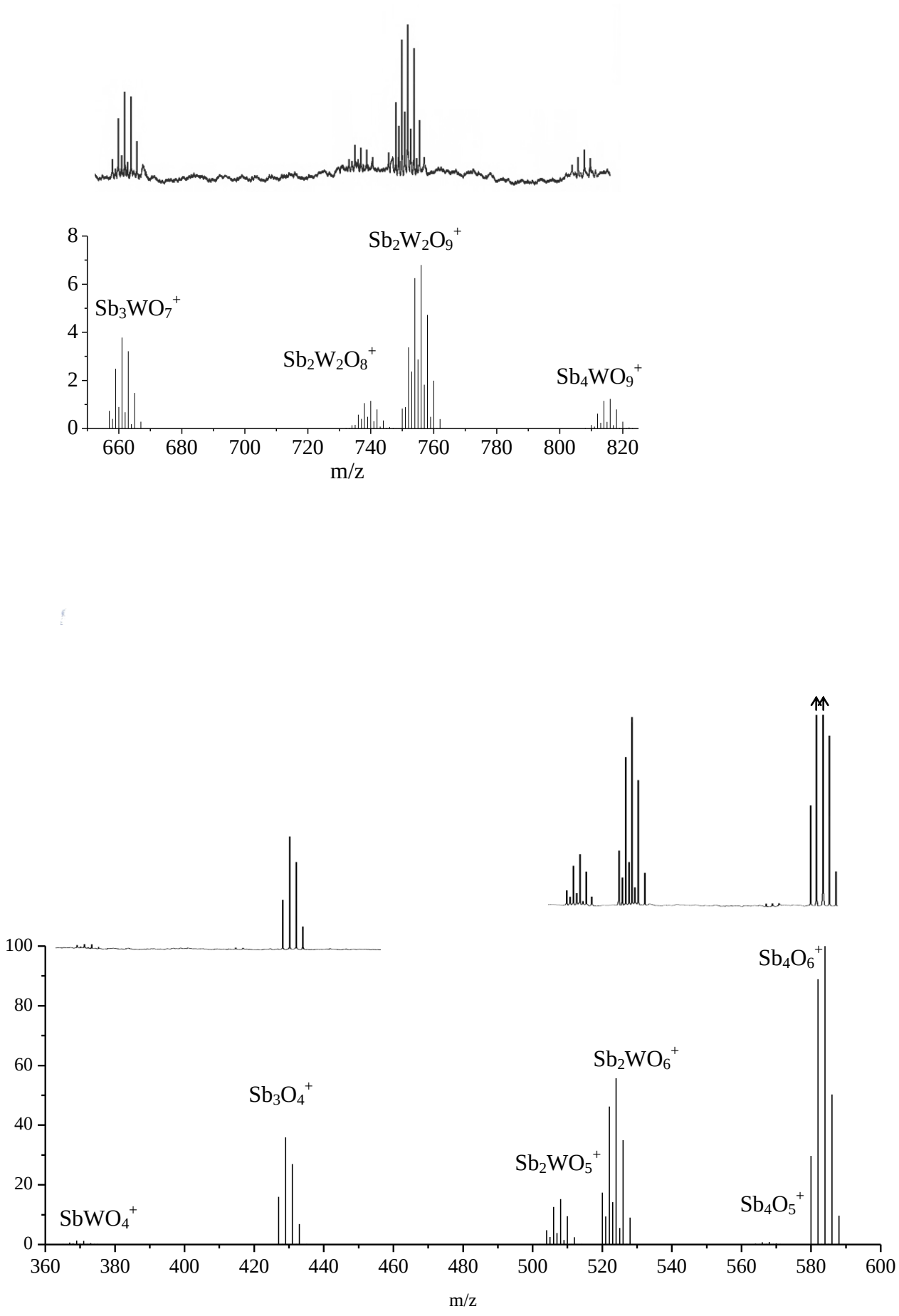

Fig. S3 Experimental and simulated mass spectra of gaseous Sb_2O_3 above solid WO_3, 1080 K, 70 eV.

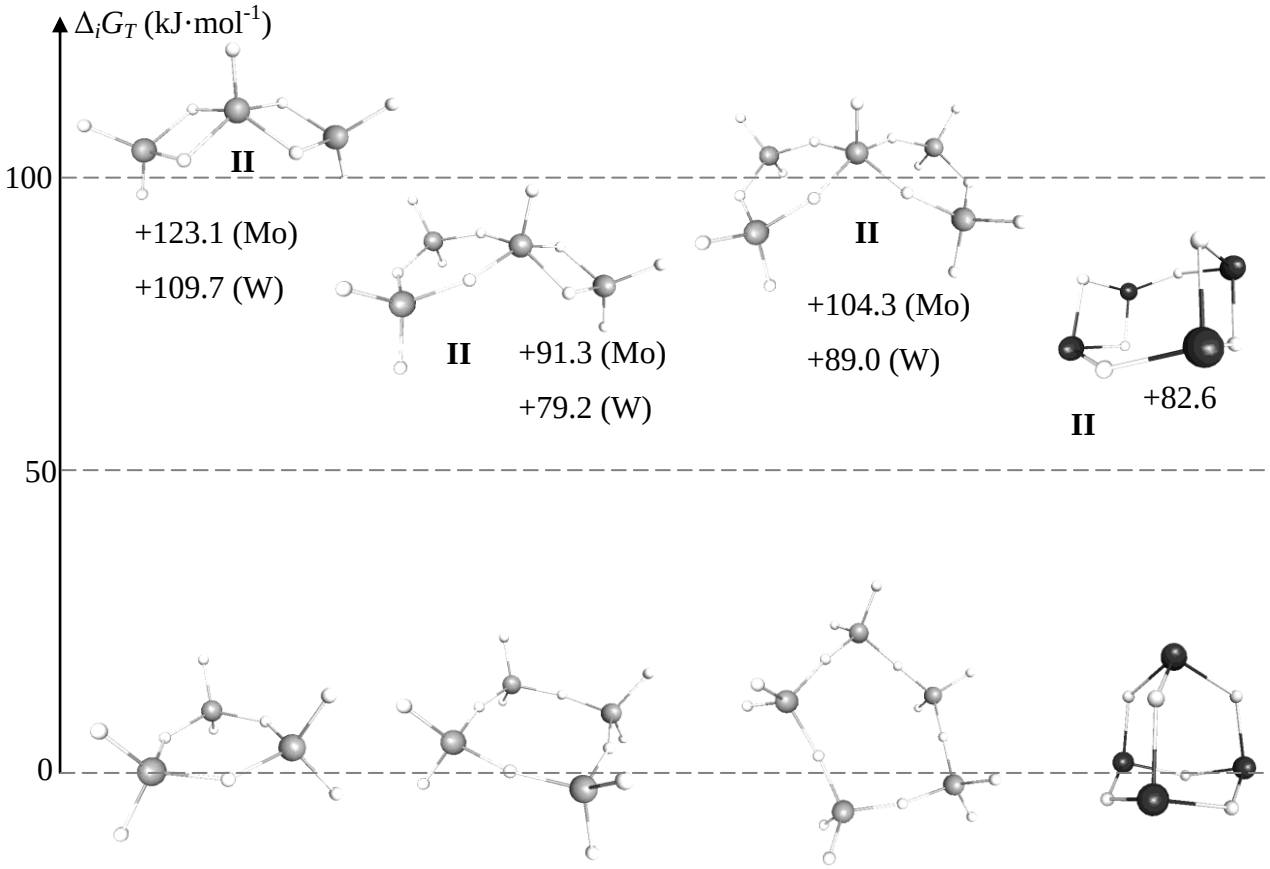

Fig. S4 Gibbs free energy of the isomer transition of $(MO_3)_x$ (x = 3-5, M = Mo, W) and Sb_4O_6 (def2-TZVP/RI-BP86) at the experimental temperatures.

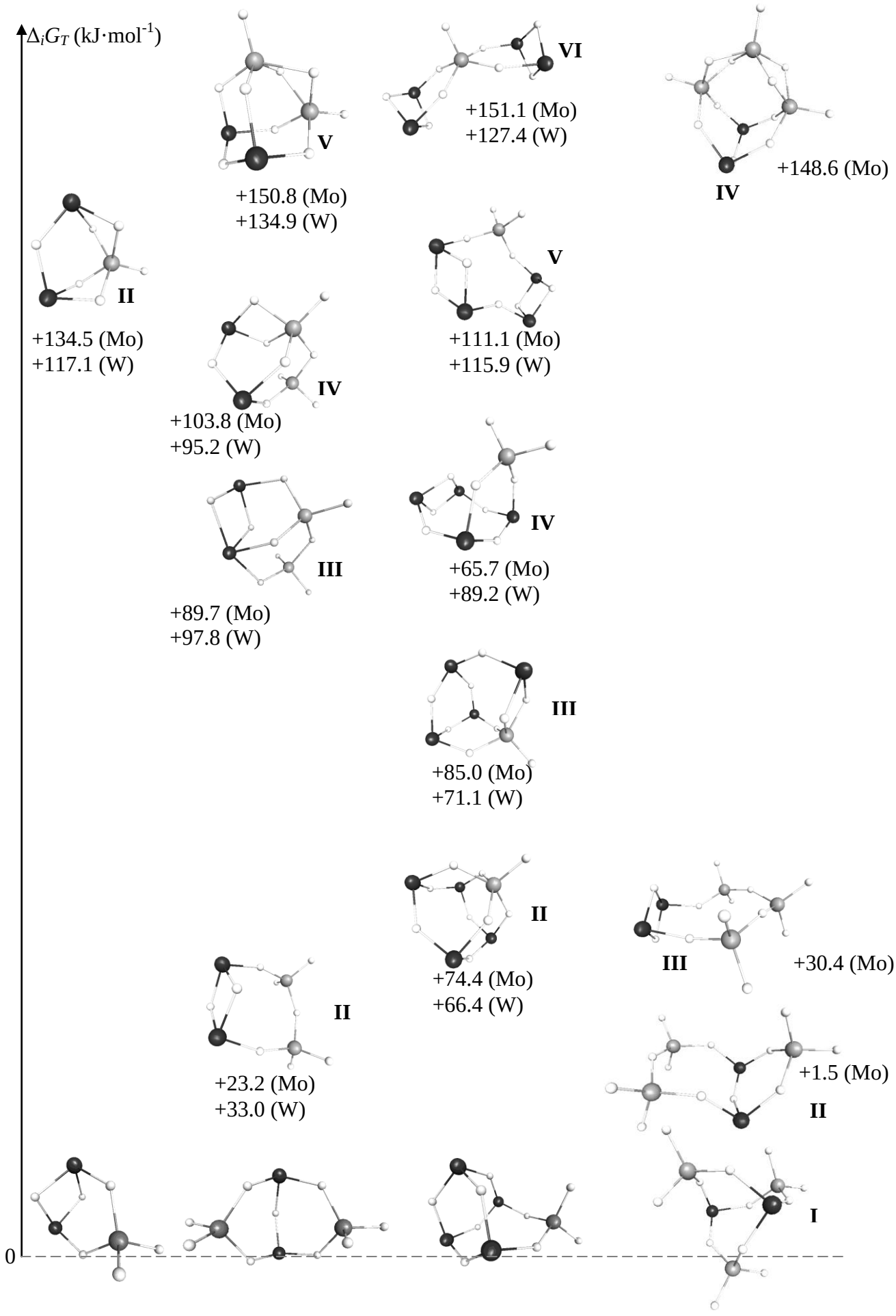

Fig. S5 Gibbs free energy of the isomer transition of Sb_2MO_6, $Sb_2M_2O_9$, Sb_4MO_9 (M = Mo, W) and $Sb_2Mo_3O_{12}$ oxides (def2-TZVP/RI-BP86) at the experimental temperatures.

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