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Supporting Information to

Photodissociation Spectroscopy of Di-Manganese Oxide Cluster Cations

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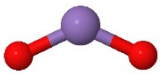
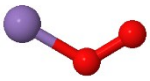
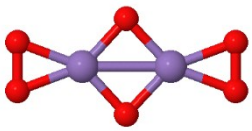
1. Determination of Frequency Scaling Factors

To obtain a set of reliable reference data for the determination of frequency scaling factors, structure optimization and vibrational frequency calculations have been performed for the neutral complexes MnO, OMnO, MnOO (with end-on bound O_2), and Mn_2O_6. These theoretically obtained values have been compared to the experimental values reported in literature. Most of the experimental data have been performed via matrix isolation IR spectroscopy. Depending on the vibrational frequency and the nature of the matrix, the influence of the matrix can lead to a more or less strong shift of the vibrational modes from the gas phase values. However, since gas phase data are scarce, the literature values in matrixes have to be used. If available the values obtained in different matrixes have been used.

Cluster	Spin	Geometry	
MnO:	$\mu = 5$	d(Mn-O) = 1.638 Å	Experimental value: 1.76 Å[1]
OMnO: 	$\mu = 3$	d(Mn-O) = 1.609 Å α(OMnO) = 129°	The structure and spin state is in agreement with a previous study using the B3LYP functional.[2]
MnOO: 	$\mu = 3$	d(Mn-O_2) = 1.839 Å d(O-O) = 1.308 Å	This isomer is found to be 3.81 eV higher in energy than the OMnO isomer. Previous studies found this isomer to be only 2.04 eV higher in energy.[2]
Mn_2O_6: 	$\mu = 0$	d(Mn-O_2) = 1.919 Å d(O-O) = 1.351 Å	A similar structure has previously been reported by Gong et al., however, using the B3LYP functional, the high spin (μ = 10) isomer has been predicted to represent the minimum energy structure.[3] This isomer is 0.82 eV higher in energy in our calculations

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$Mn_2O_4^+$ and $Mn_2O_6^+$: The structures of these clusters are discussed in detail in section 3.3 of the manuscript and Figures S2 and S3.

Table S1: Theoretically (DFT calculations obtained with the use of the software package VASP[4]) and experimentally obtained vibrational frequencies for the Mn-O and O-O stretch vibrations as well as Mn-O-Mn modes used for obtaining the frequency scaling factors given in Table 1 of the manuscript.

Mode	DFT ν / cm^{-1}	Experiment ν / cm^{-1}	Cluster	Matrix	Reference
Mn-O	928	833.1	MnO	Ar	2
		832.4		gas phase	5
		839.6			1
		830.9		Ne	6
sym. stretch	934	816.4	OMnO	Ar	2
		834.0		Ne	6
asym. stretch	1043	948	OMnO	Ar	2
		962.8		Ne	6
O-O	1181	1224.5	MnOO	Ar	2
	1193[(a)] 1186[(b)]	1157	$Mn_2O_4^+$	gas phase	this work
	1135,1118	1092	Mn_2O_6	Ar	3
	1193	1161	$Mn_2O_6^+$	gas phase	this work
	1273	1235		gas phase	this work
Mn-O-Mn and others	599[(a)] 617[(b)]	652	$Mn_2O_4^+$	gas phase	this work
	733[(a)] 704[(b)]	692			
	774[(a)] 779[(b)]	719			
	484[(a)] 466[(b)]	446			
	638	665	$Mn_2O_6^+$	gas phase	this work
	812	758			
	464	459			
	312	336			

(a) for μ = 1 isomer; (b) for μ = 7 isomer, which is +0.1 eV higher in energy than the μ = 1 isomer

1 *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; National Institute of Standards and Technology: Gaithersburg MD; Vol. http://webbook.nist.gov.
2 G. V. Chertihin; L. Andrews. *J. Phys. Chem. A* 1997, **101**, 8547.
3 Y. Gong; G. Wang; M. Zhou. *J. Phys. Chem. A* 2008, **112**, 4936.
4 G. Kresse; J. Hafner. *Phys. Rev. B* 1993, **47**, 558; G. Kresse; J. Hafner. *Phys. Rev. B* 1994, **49**, 14251; G. Kresse; J. Furthmüller. *Phys. Rev. B* 1996, **54**, 11169; G. Kresse; J. Furthmüller. *Comp. Mat. Sci.* 1996, **6**, 15.
5 R. M. Gordon; A. J. Merer. *Can. J. of Phys.* 1980, **58**, 642; A. J. Merer. *Annu. Rev. Phys. Chem.* 1989, **40**, 407.
6 Y. Gong; M. Zhou; L. Andrews. *Chem. Rev.* 2009, **109**, 6765.

2. Geometric Details of Isomeric Structures

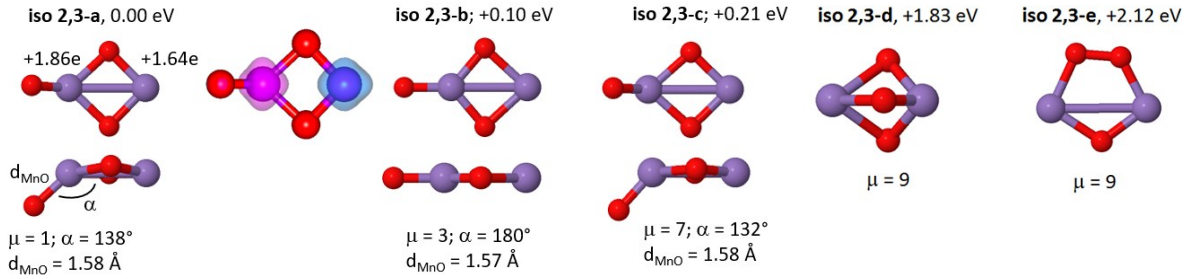

Figure S1: Geometric details of different isomeric structure of $Mn_2O_3^+$. The structures are shown in front and top view. μ denotes the number of unpaired electrons, α the angle of the terminal O relative to the Mn_2O_2 plane, and *d* the bond length. The numbers above the Mn atoms correspond to the Bader charges located on the Mn atoms. Also shown is the spin density difference isosurface (difference of majority and minority spin density, shown in pink and blue) of iso 2,3-a (encompassing 98% of the total spin density). Mn and O atoms are depicted by purple and red spheres, respectively.

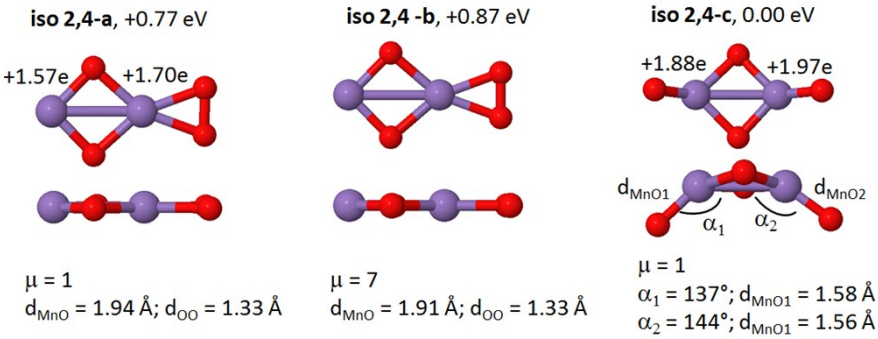

Figure S2: Geometric details of different isomeric structure of $Mn_2O_4^+$. The structures are shown in front and top view. μ denotes the number of unpaired electrons, α the angle of the terminal O relative to the Mn_2O_2 plane, and *d* the bond length. The numbers above the Mn atoms correspond to the Bader charges located on the Mn atoms. Mn and O atoms are depicted by purple and red spheres, respectively.

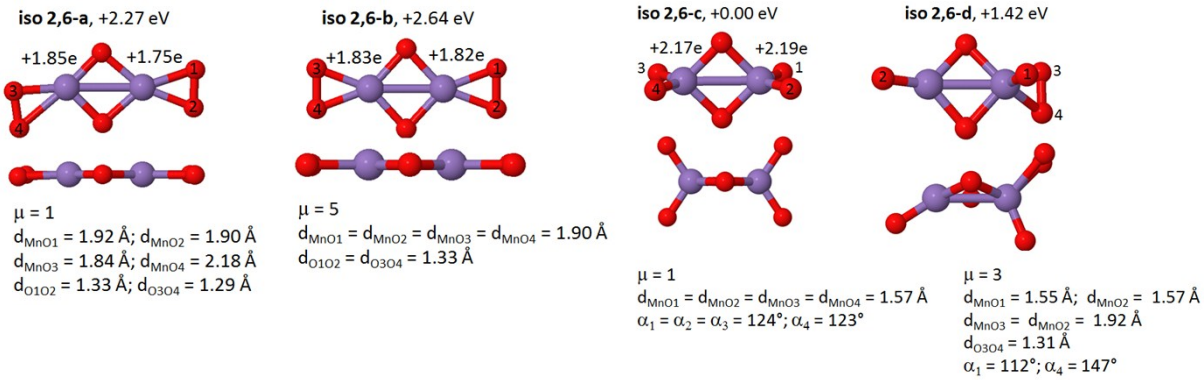

Figure S3: Geometric details of different isomeric structure of $Mn_2O_6^+$. The structures are shown in front and top view. μ denotes the number of unpaired electrons, α the angle of the terminal O relative to the Mn_2O_2 plane, and *d* the bond length. The numbers above the Mn atoms correspond to the Bader charges located on the Mn atoms. Mn and O atoms are depicted by purple and red spheres, respectively.

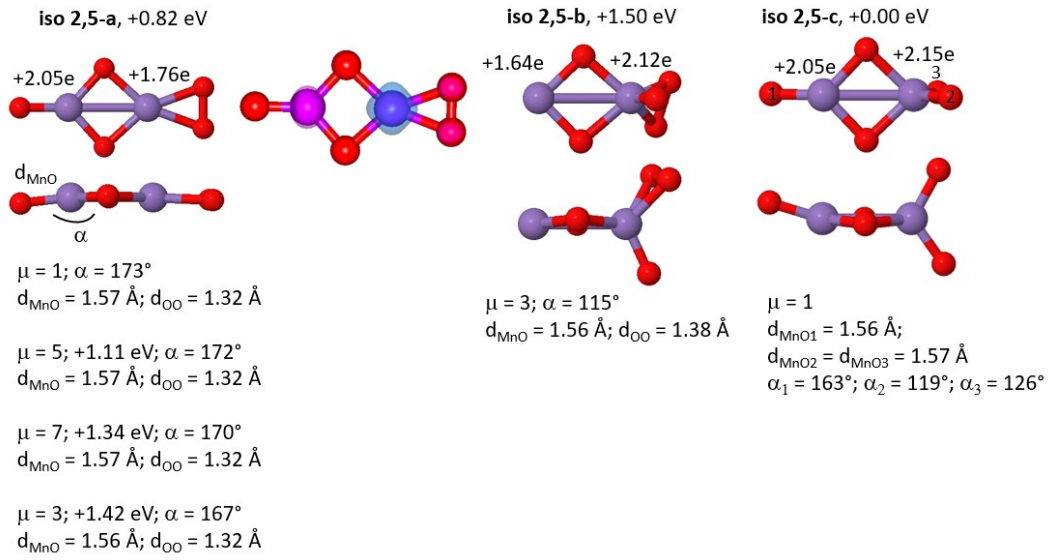

Figure S4: Geometric details of different isomeric structure of $Mn_2O_5^+$. The structures are shown in front and top view. μ denotes the number of unpaired electrons, α the angle of the terminal O relative to the Mn_2O_2 plane, and *d* the bond length. The numbers above the Mn atoms correspond to the Bader charges located on the Mn atoms. Also shown is the spin density difference isosurface (difference of majority and minority spin density, shown in pink and blue) of iso 2,5-a (encompassing 98% of the total spin density). Mn and O atoms are depicted by purple and red spheres, respectively.

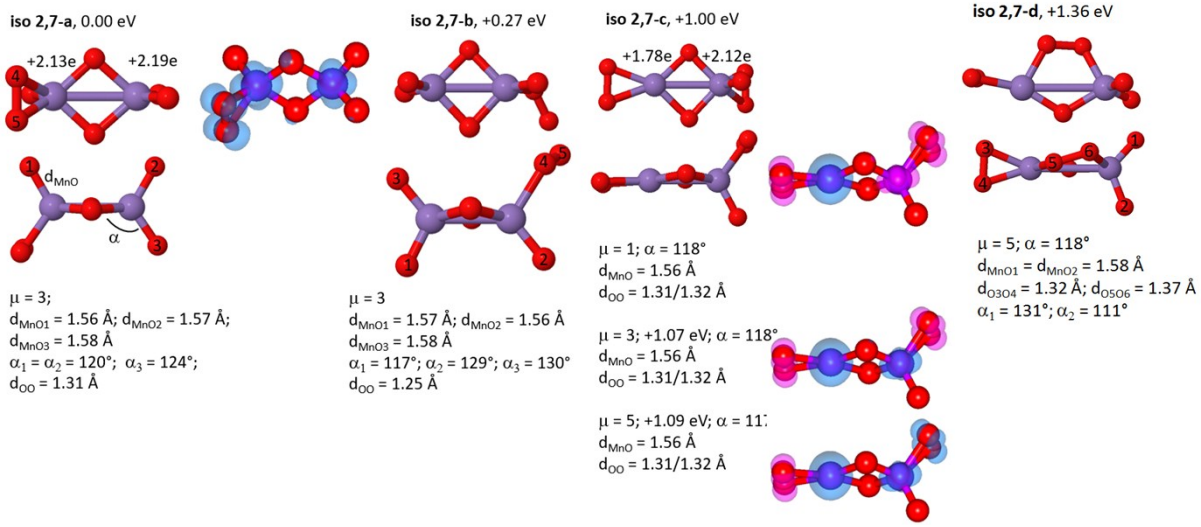

Figure S5: Geometric details of different isomeric structure of $Mn_2O_7^+$. The structures are shown in front and top view. μ denotes the number of unpaired electrons, α the angle of the terminal O relative to the Mn_2O_2 plane, and *d* the bond length. The numbers above the Mn atoms correspond to the Bader charges located on the Mn atoms. Also shown is the spin density difference isosurface (difference of majority and minority spin density, shown in pink and blue) of iso 2,7-a as well as for iso 2,7-c (μ = 1,3,5) (encompassing 98% of the total spin density). Mn and O atoms are depicted by purple and red spheres, respectively.