Supporting Information

Electron Binding Energy Spectra of Al_nMo^- Clusters: Measurements, Calculations and Theoretical Analysis

Paulo H. Acioli[1], Xinxing Zhang[2], Kit H. Bowen Jr.[3*] and Julius Jellinek[4*]

[1]Department of Physics, Northeastern Illinois University, Chicago, Illinois 60625, USA

[2]Collaborative Innovation Center of Chemical Sciences and Engineering, College of Chemistry, Nankai University, Tianjin 300071, China

[3]Departments of Chemistry and Materials Science, Johns Hopkins University, Baltimore, Maryland 21218, USA

[4]Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60349, USA

1. Results of tests

Table S1. Calculated DFT (BPW91, PBE and BP86) and measured (Exp) results for Mo, Mo_2, Al, and Al_2. IP, IP_a, EA and r_e denote ionization potential, adiabatic ionization potential, electron affinity and interatomic equilibrium distance, respectively.

System	Property	BPW91	PBE	BP86	Exp
Mo	IP(eV)	7.604	7.573	7.731	7.0924[1]
	EA(eV)	0.355	0.496	0.722	0.7473[2]
Mo_2	BE(eV/atom)	1.415	1.643	1.789	2.24[3]
	IP_a (eV)	7.122	7.166	7.324	6.95[3]
	EA(eV)	0.753	0.762	0.904	> 1.0[4]
	r_e (Å)	1.984	1.983	1.985	1.94[3]
Al	IP (eV)	6.060	6.169	6.243	5.984[5]
	EA(eV)	0.280	0.270	0.335	0.441[6]
Al_2	BE(eV/atom)	0.677	0.723	0.673	0.67[7]
	IP_a (eV)	6.014	5.922	5.941	5.989[8]
	EA(eV)	1.467	1.469	1.540	1.46[9]
	r_e (Å)	2.571	2.571	2.580	2.701[7]

[1] Rayner, D. M.; Mitchell, S. A.; Bourne, O. L.; Hackett, P. A. First-Ionization Potential of Niobium and Molybdenum by Double-Resonance, Field-Ionization Spectroscopy. *J. Opt. Soc. Am. B* **1987**, *4*, 900-905.

[2] Bilodeau, R. C.; Scheer, M.; Haugen, H. K. Infrared Laser Photodetachment of Transition Metal Negative Ions: Studies on Cr^-, Mo^-, Cu^- and Ag^-. *J. Physics B: Atom. Mol. Opt. Phys.* **1998**, *31*, 3885-3892.

[3] Simard, B.; Lebeault-Dorget, M.; Marijnissen, A.; ter Meulen, J. J. Photoionization Spectroscopy of Dichromium and Dimolybdenum: Ionization Potentials and Bond Energies. *J. Chem. Phys.* **1998**, *108*, 9668-9674.

[4] Balasubramanian, K. Spectroscopic Properties of Mo_2^- and Mo_2^+. *Chem. Phys. Lett.* **2002**, *365*, 413-420.

[5] Moore, C. E. Atomic Energy Levels and Other Spectroscopic Data - NIST Page. *Natl. Bur. Stand. Circ.* 467, US GPO, Washington, D.C., 1949, 1952.

[6] Hotop H.; Lineberger, W. C. Binding Energies in Atomic Negative Ions: II. *J. Phys. Chem. Ref. Data* **1985**, *14*, 731-750.

[7] Fu, Z.; Lemire, G. W.; Bishea, G. A.; Morse, M. D. Spectroscopy and Electronic Structure of Jet-Cooled Al_2. *J. Chem. Phys.* **1990**, *93*, 8420-8441.

[8] Harrington J. E.; Weisshaar, J. C. Adiabatic Ionization Potential of Al_2 and Vibrational Spectrum of the $X^2\Sigma_g^2$ State of Al_2^+. *J. Chem. Phys.* **1990**, *93*, 854-855.

[9] Li, X.; Wu, H.; Wang, X.-B.; Wang, L.-S. *s-p* Hybridization and Electron Shell Structures in Aluminum Clusters: A Photoelectron Spectroscopy Study. *Phys. Rev. Lett.* **1998**, *81*, 1909-1912.

The comparison of the calculated and measured results, especially those for electron affinities, points to BP86 as the optimal choice for the exchange-correlation functional.

2. Results of calculations for the lowest energy structures of Al_nMo^-, n=3-5 and 7, the Mo and Al atoms, and the lowest energy structures of Al_n^-, n=4 and 5.

Table S2. Negatives of the upper Kohn-Sham (KS) eigenenergies ($-\varepsilon_i$) and their corresponding correction terms (Δ_i)[10] and electron binding energies (EBE_i) for the lowest energy (C_{3v}) structure of the Al_3Mo^- cluster. All values are in eV. Bold numbers/letters indicate the part of the calculated spectrum whose EBE_i fall under the measured EBE spectrum.

Cluster	i	Eigenstate label and occupancy	$-\varepsilon_i$	Δ_i	EBE_i
Al_3Mo^-	**1**	$\mathbf{e^2(\beta)}$	**0.249**	**1.980**	**2.229**
	2	$\mathbf{a_1^1(\alpha)}$	**0.345**	**1.986**	**2.331**
	3	$\mathbf{e^2(\alpha)}$	**0.586**	**2.000**	**2.586**
	4	$\mathbf{e^2(\alpha)}$	**0.707**	**2.008**	**2.714**
	5	$\mathbf{a_1^1(\alpha)}$	**0.757**	**2.011**	**2.768**
	6	$\mathbf{a_1^1(\beta)}$	**0.847**	**2.016**	**2.862**
	7	$\mathbf{a_1^1(\alpha)}$	**1.216**	**2.034**	**3.250**
	8	$a_1^1(\beta)$	3.232	2.137	5.370

[10] Jellinek, J.; Acioli, P. H. Converting Kohn−Sham Eigenenergies into Electron Binding Energies. *J. Chem. Phys.* **2003,** *118*, 7783-7796.

The listed EBE_i values calculated with the orbital-specific corrections Δ_i are used in the main text.

Table S3. The same as Table S2, but for the lowest energy (C_{2v}) structure of the Al_4Mo^- cluster.

Cluster	i	Eigenstate label and occupancy	$-\varepsilon_i$	Δ_i	EBE_i	EBE_i (constant correction)
Al_4Mo^-	**1**	**$b_1^1(\beta)$**	**0.246**	**1.885**	**2.131**	**2.131**
	2	**$b_1^1(\alpha)$**	**0.514**	**1.891**	**2.405**	**2.399**
	3	**$a_1^1(\alpha)$**	**0.536**	**1.892**	**2.428**	**2.421**
	4	**$b_2^1(\beta)$**	**0.655**	**1.895**	**2.549**	**2.540**
	5	**$a_1^1(\beta)$**	**0.717**	**1.896**	**2.613**	**2.602**
	6	**$b_2^1(\alpha)$**	**0.812**	**1.899**	**2.711**	**2.697**
	7	**$a_1^1(\alpha)$**	**0.912**	**1.901**	**2.813**	**2.797**
	8	**$a_1^1(\beta)$**	**1.391**	**1.915**	**3.306**	**3.276**
	9	**$a_2^1(\beta)$**	**1.516**	**1.918**	**3.435**	**3.401**
	10	$a_1(\alpha)$	1.585	1.920	3.506	3.470
	11	$a_2(\alpha)$	1.601	1.921	3.522	3.486
	12	$a_1(\beta)$	2.700	1.956	4.656	4.585
	13	$a_1(\alpha)$	2.963	1.965	4.928	4.848

The EBE_i values calculated with the constant correction Δ_1 (correction for the HOMO KS eigenenergy) and listed in the last column of the table are used in the main text.

Table S4. The same as Table S2, but for the lowest energy (C_{4v}) structure of the Al_5Mo^- cluster.

Cluster	i	Eigenstate label and occupancy	$-\varepsilon_i$	Δ_i	EBE_i	EBE_i (constant correction)
Al_5Mo^-	**1**	$\mathbf{a_1^2}$	**0.269**	**1.895**	**2.163**	**2.163**
	2	$\mathbf{b_2^2}$	**0.743**	**1.900**	**2.643**	**2.638**
	3	$\mathbf{a_1^2}$	**0.978**	**1.902**	**2.880**	**2.873**
	4	$\mathbf{e^4}$	**1.345**	**1.905**	**3.250**	**3.239**
	5	b_1^2	1.898	1.909	3.807	3.792
	6	a_1^2	3.721	1.920	5.641	5.616

The EBE_i values calculated with the constant correction Δ_1 (correction for the HOMO KS eigenenergy) and listed in the last column of the table are used in the main text.

Table S5. The same as Table S2, but for the lowest energy (C_{2v}) structure of the Al_7Mo^- cluster.

Cluster	i	Eigenstate label and occupancy	$-\varepsilon_i$	Δ_i	EBE_i	EBE_i (constant correction)
Al_7Mo^-	**1**	$\mathbf{a_2^2}$	**0.894**	**1.750**	**2.644**	**2.644**
	2	$\mathbf{b_1^2}$	**1.109**	**1.753**	**2.862**	**2.859**
	3	$\mathbf{a_1^2}$	**1.376**	**1.756**	**3.132**	**3.126**
	4	$\mathbf{a_1^2}$	**1.377**	**1.756**	**3.133**	**3.127**
	5	$\mathbf{b_1^2}$	**1.484**	**1.758**	**3.242**	**3.234**
	6	b_2^2	1.811	1.762	3.573	3.561
	7	a_1^2	1.960	1.765	3.724	3.710
	8	a_1^2	3.232	1.787	5.019	4.982

The EBE_i values calculated with the constant correction Δ_1 (correction for the HOMO KS eigenenergy) and listed in the last column of the table are used in the main text.

Table S6. The same as Table S2, but for the Mo atom.

Atom	i	Eigenstate label and occupancy	$-\varepsilon_i$	Δ_i	EBE_i
Mo	1	$4d^5(\alpha)$	4.628	3.103	7.731
	2	$5s^1(\alpha)$	4.858	3.167	8.026

The listed EBE_i values calculated with the orbital-specific corrections Δ_i are used in the main text.

Table S7. The same as Table S2, but for the Al atom.

Atom	i	Eigenstate label and occupancy	$-\varepsilon_i$	Δ_i	EBE_i
Al	1	$3p^1(\alpha)$	3.093	3.150	6.243
	2	$3s^1(\beta)$	7.514	3.363	10.664
	3	$3s^1(\alpha)$	8.074	3.390	11.224

The listed EBE_i values calculated with the orbital-specific corrections Δ_i are used in the main text.

Table S8. The same as Table S2, but for the lowest energy (D_{2h}) structure of the Al_4^- cluster.

Cluster	i	Eigenstate label and occupancy	$-\varepsilon_i$	Δ_i	EBE_i
Al_4^-	**1**	$\mathbf{b_{3g}^1(\beta)}$	**0.214**	**2.022**	**2.236**
	2	$\mathbf{b_{3u}^1(\beta)}$	**0.253**	**2.025**	**2.278**
	3	$\mathbf{b_{3u}^1(\alpha)}$	**0.285**	**2.027**	**2.312**
	4	$\mathbf{b_{3g}^1(\alpha)}$	**0.339**	**2.030**	**2.369**
	5	$\mathbf{a_g^1(\alpha)}$	**1.296**	**2.084**	**3.380**
	6	$a_g^1(\beta)$	1.533	2.095	3.628
	7	$b_{2u}^1(\beta)$	3.435	2.179	5.614
	8	$b_{2u}^1(\alpha)$	3.735	2.187	5.922

The listed EBE_i values calculated with the orbital-specific corrections Δ_i are used in the main text.

Table S9. The same as Table S2, but for the lowest energy (C_s) structure of the Al_5^- cluster.

Cluster	i	Eigenstate label and occupancy	$-\varepsilon_i$	Δ_i	EBE_i	EBE_i (constant correction)
Al_5^-	**1**	**A'^2**	**0.459**	**1.830**	**2.289**	**2.289**
	2	**A'^2**	**0.817**	**1.840**	**2.657**	**2.647**
	3	**A''^2**	**0.912**	**1.842**	**2.754**	**2.742**
	4	A'^2	2.028	1.873	3.901	3.858
	5	A'^2	2.977	1.900	4.877	4.807
	6	A'^2	4.376	1.941	6.316	6.206
	7	A'	5.423	1.970	7.393	7.253

The EBE_i values calculated with the constant correction Δ_1 (correction for the HOMO KS eigenenergy) and listed in the last column of the table are used in the main text.

3. Normal mode frequencies, harmonic zero-point energies, and room-temperature thermal energies.

Table S10. Normal mode frequencies ν_i (in cm^{-1}) for the lowest energy structures of Al_nMo^-, n=3,4,5 and 7, the C_{4v} transition state (TS) configuration of Al_4Mo^-, and the C_{2v} TS configuration of Al_5^-.

i	Al_3Mo^-	Al_4Mo^-	Al_5Mo^-	Al_7Mo^-	Al_4Mo^-(TS)	Al_5^-(TS)
			ν_i			
1	142.51	48.87	47.28	74.37	35.35*i*	28.93*i*
2	142.51	151.79	47.28	101.26	149.53	36.45
3	170.63	156.53	85.71	115.55	178.86	109.11
4	298.95	171.73	97.84	137.07	178.86	155.74
5	298.95	187.27	143.39	152.53	216.01	221.92
6	343.38	253.60	143.39	165.49	246.65	227.48
7		297.54	151.16	166.25	308.96	283.27
8		327.92	261.63	197.19	308.96	339.20
9		344.90	285.00	206.41	338.10	351.83
10			330.26	222.55		
11			330.26	226.91		
12			334.84	233.96		
13				235.10		
14				244.08		
15				266.72		
16				309.27		
17				316.85		
18				358.35		

Table S11. Harmonic zero-point energies $E_0 = 0.5h\sum_i \nu_i$ and room-temperature (T=300 K) thermal vibrational energies $E_T = fkT$ (all in eV) for the lowest energy structures of Al_nMo^-, n=3,4,5 and 7, the C_{4v} TS configuration of Al_4Mo^-, and the C_{2v} TS configuration of Al_5^-. h is Planck's constant, f is the number of vibrational modes with real-valued frequencies, and k is Boltzmann's constant.

	Al_3Mo^-	Al_4Mo^-	Al_5Mo^-	Al_7Mo^-	Al_4Mo^-(TS)	Al_5^-(TS)
E_0	0.087	0.120	0.140	0.231	0.119	0.107
E_T	0.155	0.232	0.310	0.465	0.207	0.207

4. Crossing of two electronic states of the Al_4Mo^- cluster.

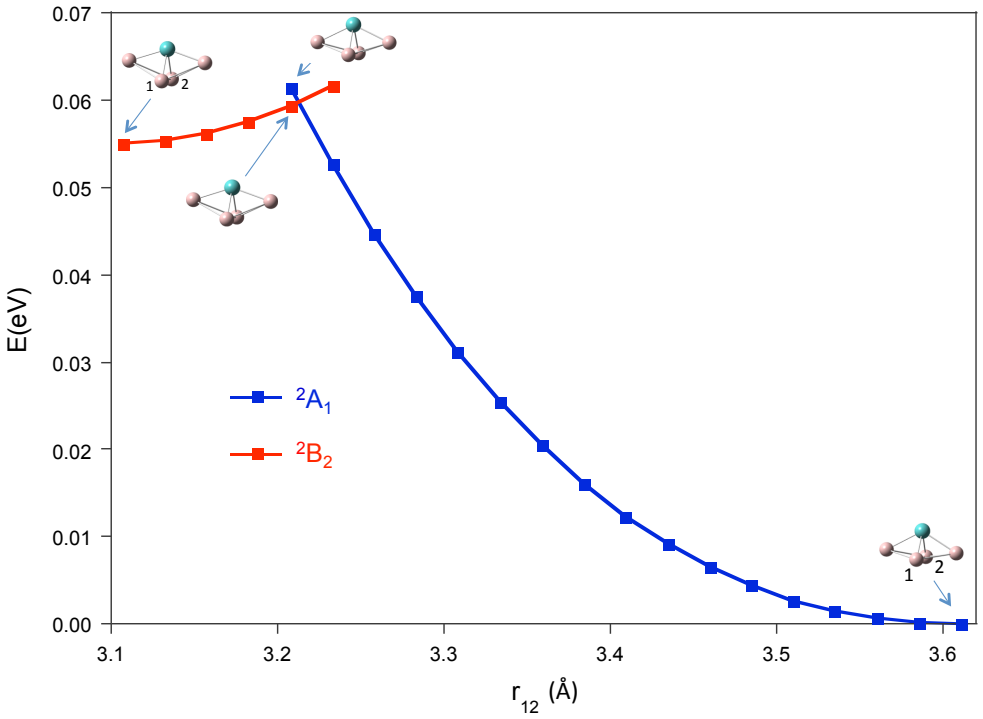

Figure S1. Crossing of the $^2A_1$ and $^2B_2$ electronic states corresponding to two C_{2v} forms of the Al_4Mo^- cluster (see the main text for details).

The two graphs were obtained through constrained energy minimizations on grids of r_{12} distances (distances between atoms 1 and 2) starting from the corresponding equilibrium structures represented by the bottoms of the two graphs. Near the crossing point the constrained minimizations also involved fixing the corresponding electronic states. The energy at the crossing point (r_{12}=3.21 Å) obtained through interpolation is just 0.060 eV above the equilibrium energy of the most stable form of the cluster.