Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information (SI)

Predicting the Structural Evolution of Ge_n ($3 \leq n \leq 20$) Clusters: an Anion Photoelectron Spectroscopy Simulation

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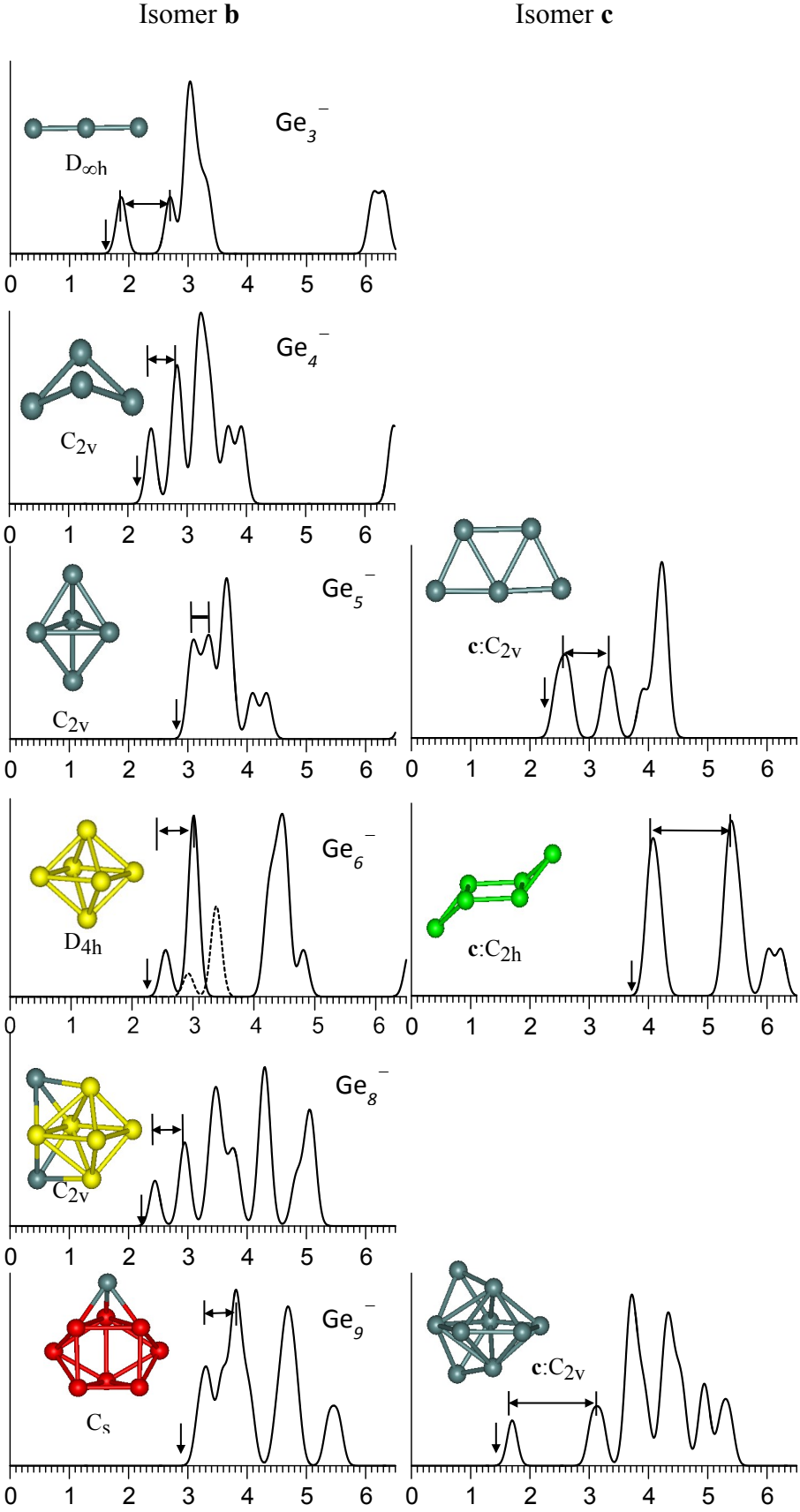
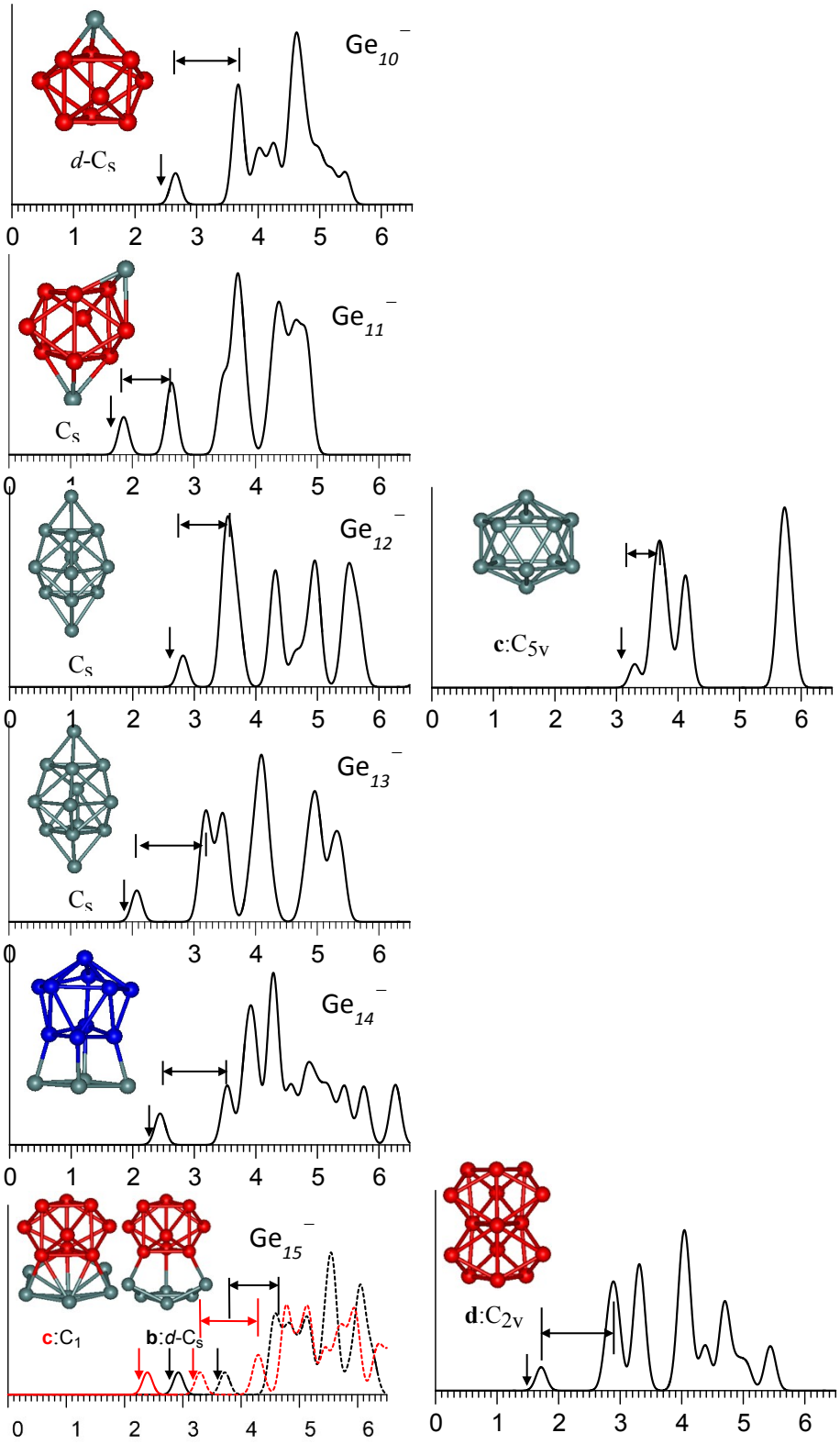

Isomer **b**
Isomer **c**
Ge_3^-
$D_{\infty h}$
Ge_4^-
C_{2v}
Ge_5^-
C_{2v}
c:C_{2v}
Ge_6^-
D_{4h}
c:C_{2h}
Ge_8^-
C_{2v}
Ge_9^-
C_s
c:C_{2v}
0 1 2 3 4 5 6


Ge10−
d-Cs
Ge11−
Cs
Ge12−
Cs
c:C5v
Ge13−
Cs
Ge14−
Ge15−
c:C1
b:d-Cs
d:C2v
0 1 2 3 4 5 6

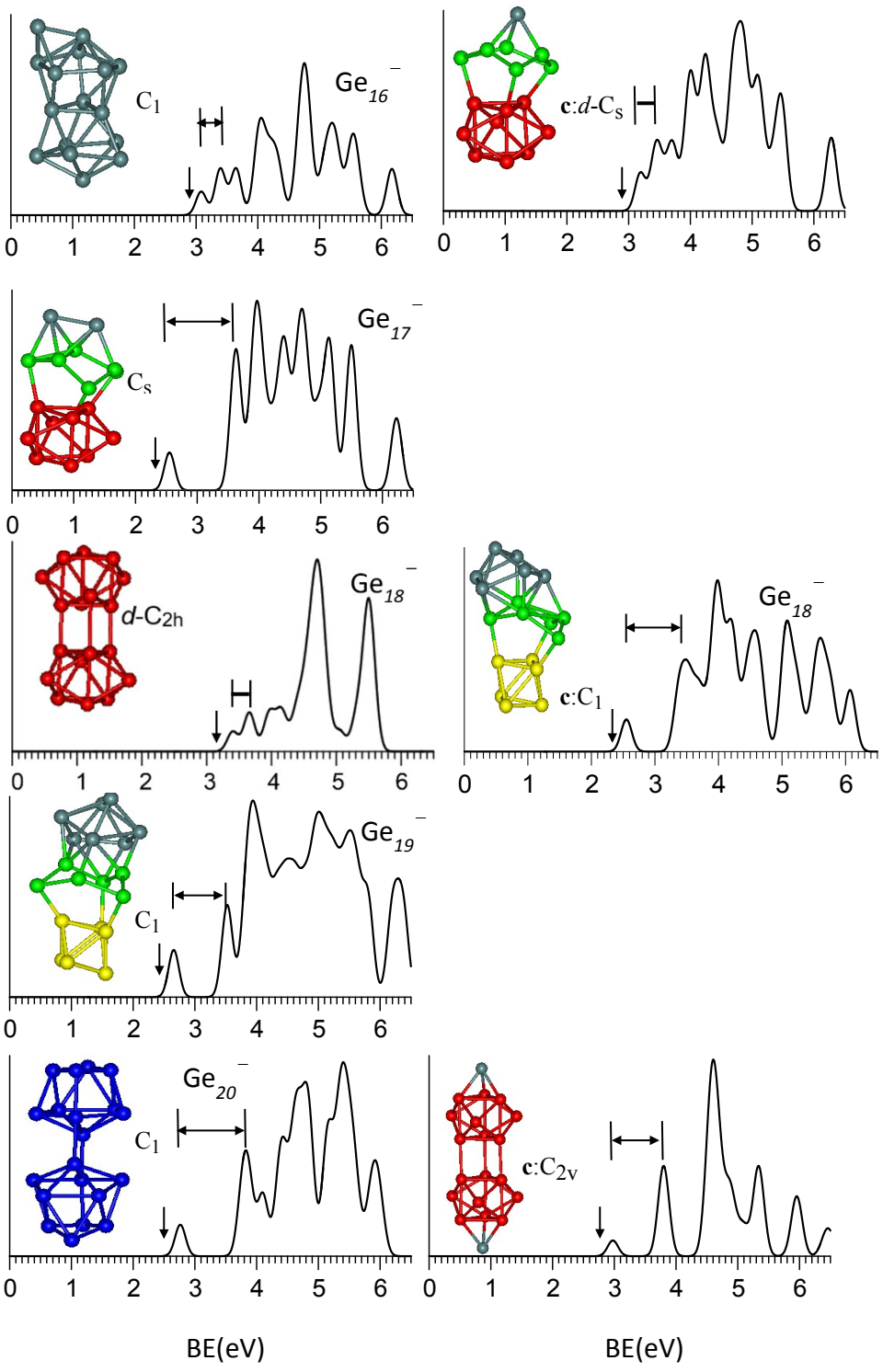
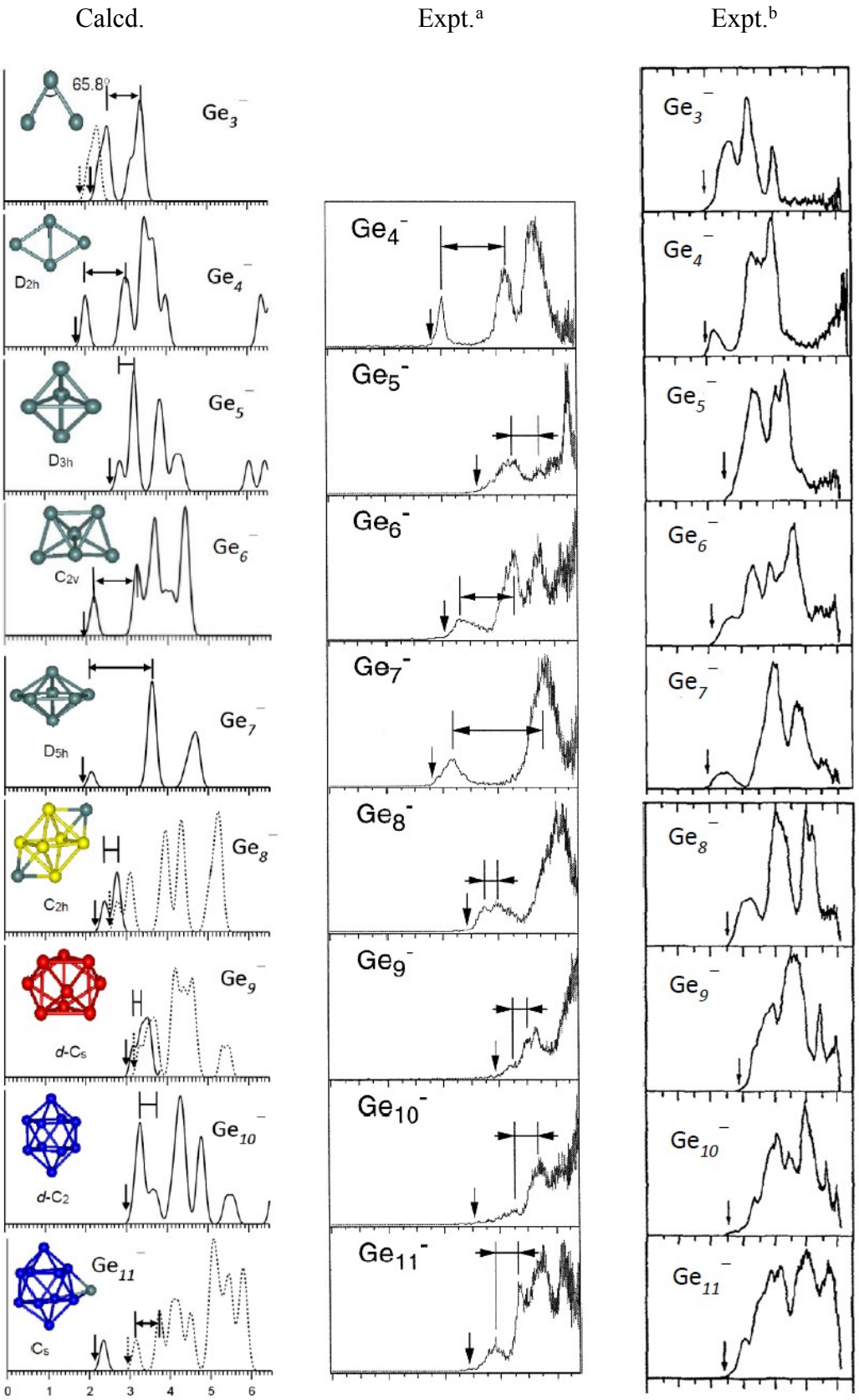


Figure S1. Simulated anion photoelectron spectra for low-lying isomers (**b** and **c**) of Ge_n^- ($3 \leq n \leq 20$), as in Figure 1.


Calcd.
Expt.[a]
Expt.[b]
65.8°
Ge3−
D2h
Ge4−
D3h
Ge5−
C2v
Ge6−
D5h
Ge7−
C2h
Ge8−
d-Cs
Ge9−
d-C2
Ge10−
Cs
Ge11−
Ge4-
Ge5-
Ge6-
Ge7-
Ge8-
Ge9-
Ge10-
Ge11-
0 1 2 3 4 5 6

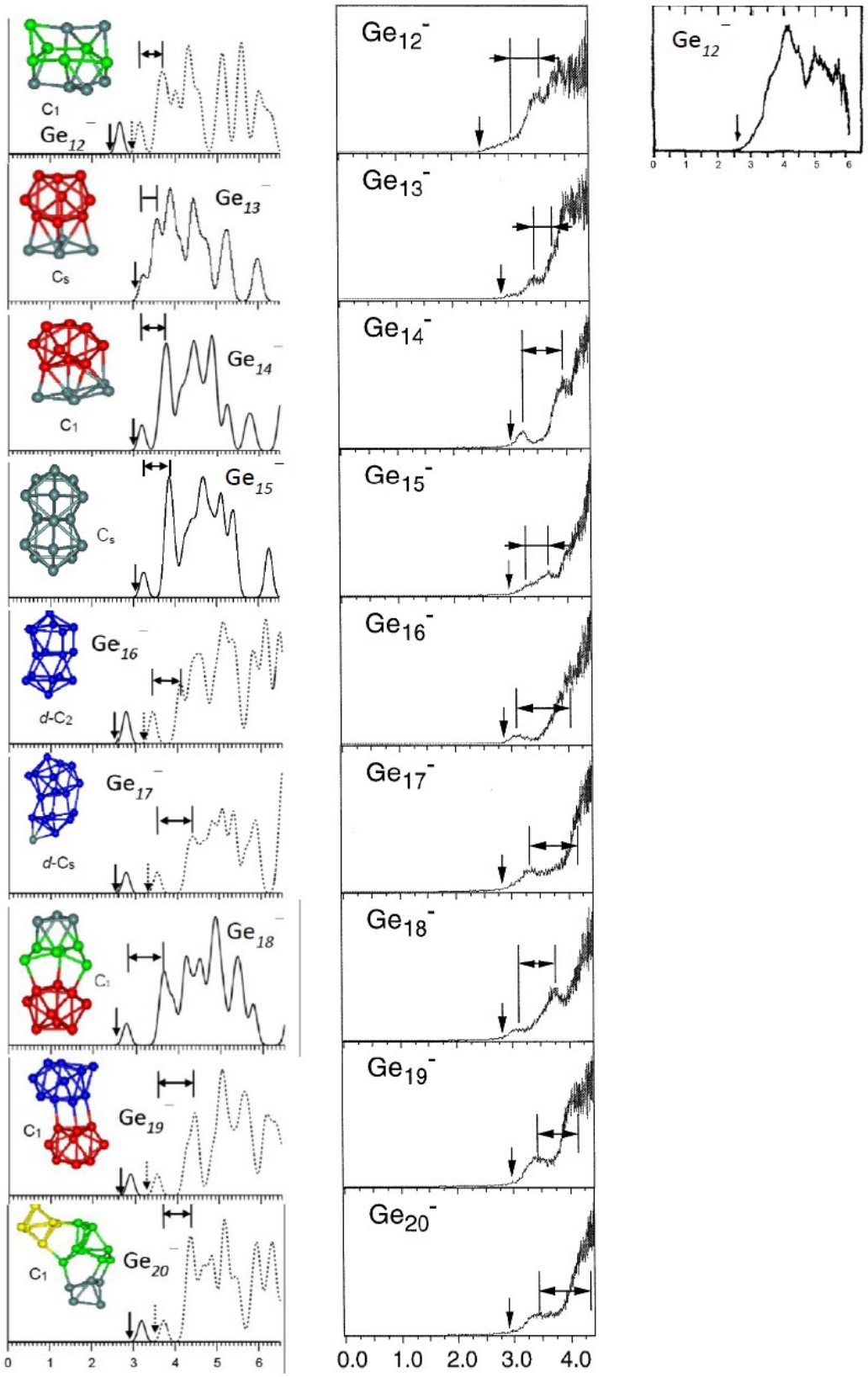

C1
Ge12−
Cs
Ge13−
C1
Ge14−
Cs
Ge15−
d-C2
Ge16−
d-Cs
Ge17−
C1
Ge18−
C1
Ge19−
C1
Ge20−
0 1 2 3 4 5 6
Ge12-
Ge13-
Ge14-
Ge15-
Ge16-
Ge17-
Ge18-
Ge19-
Ge20-
0.0 1.0 2.0 3.0 4.0
Ge12−
0 1 2 3 4 5 6

Figure S2. Simulated anion photoelectron spectra for the most likely isomers **a** of Ge_n^- ($3 \le n \le 20$) displayed side-by-side with experimental spectra retrieved from the literatures (a: ref.[1]; b: ref.[2]).

Table S1. Calculated total energy (in Hartree) for low-lying isomers of Ge_n^- ($3 \le n \le 20$) at the PBEPBE/6-31+G(d) level. The numbers in bold are the lowest-energy.

	Isomers		
Ge_n^-	**a**	**b**	**c**
Ge_3^-	**-6224.0270911**	-6223.9944786	—
Ge_4^-	**-8298.7510749**	-8298.7478876	—
Ge_5^-	**-10373.4993225**	-10373.4882103	-10373.4337560
Ge_6^-	-12448.2230418	**-12448.2289249**	-12448.1161525
Ge_7^-	**-14522.9616085**	—	—
Ge_8^-	**-16597.6487733**	-16597.6430033	—
Ge_9^-	**-18672.4017250**	-18672.3850443	-18672.3822507
Ge_{10}^-	-20747.1382428	**-20747.1461483**	—
Ge_{11}^-	**-22821.8419601**	-22821.8316704	—
Ge_{12}^-	-24896.5470716	**-24896.5679963**	-24896.5467564
Ge_{13}^-	**-26971.3069783**	-26971.2724342	—
Ge_{14}^-	**-29046.0429485**	-29046.0355122	—
Ge_{15}^-	**-31120.7925017**	-31120.7710081	-31120.7768035
Ge_{16}^-	-33195.5014249	**-33195.5081694**	-33195.5011379
Ge_{17}^-	**-35270.2311995**	-35270.2158062	—
Ge_{18}^-	-37344.9467376-	**37344.9514816**	-37344.9404279
Ge_{19}^-	-39419.6617534	**-39419.6691929**	—
Ge_{20}^-	-41494.3712309	**-41494.3852321**	-41494.3834041

Table S2. Relative stabilities (in eV) of Ge_n^- ($3 \leq n \leq 20$) with respect to the lowest-energy anion isomers as listed in Table S1.

	Isomers				
Ge_n^-	**a**	**b**	**c**	ADE(eV)[1]	HOMO–LUMO gap (eV)[2]
Ge_3^-	**0.00**	0.89	—	1.70(**b**)	0.9(**b**)
Ge_4^-	**0.00**	0.09	—	2.20(**b**)	0.3(**b**)
Ge_5^-	**0.00**	0.30	1.78	2.88(**b**)/2.29(**c**)	0.3(**b**)/0.8(**c**)
Ge_6^-	0.16	**0.00**	3.07	2.30(**b**)/3.83(**c**)	0.4(**b**)/1.3(**c**)
Ge_7^-	—	—	—		—
Ge_8^-	**0.00**	0.16	—	2.29(**b**)	0.5(**b**)
Ge_9^-	**0.00**	0.45	0.53	3.00(**b**)/1.52(**c**)	0.6(**b**)/1.5(**c**)
Ge_{10}^-	0.22	**0.00**	—	2.47(**b**)	1.0(**b**)
Ge_{11}^-	**0.00**	0.28	—	1.66(**b**)	0.7(**b**)
Ge_{12}^-	0.57	**0.00**	0.58	2.62(**b**)/3.10(**c**)	0.8(**b**)/0.4(**c**)
Ge_{13}^-	**0.00**	0.94	—	1.90(**b**)	1.1(**b**)
Ge_{14}^-	**0.00**	0.20	—	2.26(**b**)	1.1(**b**)
Ge_{15}^-	**0.00**	0.43	0.58	*s*-2.70, *t*-3.50(**b**)	0.8(**b**)
				s-2.18, *t*-3.10(**c**)	1.0(**c**)
				1.51(**d**)[3]	1.2(**d**)
Ge_{16}^-	0.18	**0.00**	0.19	2.90(**b**)/3.00(**c**)	0.3(**b**)/0.3(**c**)
Ge_{17}^-	**0.00**	0.42	—	2.38(**b**)	1.1(**b**)
Ge_{18}^-	0.13	**0.00**	0.30	3.20(**b**)/2.37(**c**)	0.3(**b**)/1.0(**c**)
Ge_{19}^-	0.20	**0.00**	—	2.46(**b**)	1.0(**b**)
Ge_{20}^-	0.38	**0.00**	0.05	2.60(**b**)/2.80(**c**)	1.1(**b**)/0.8(**c**)

[1]Calculated adiabatic detachment energy (ADE) for anion isomers of **b** and **c** based on simulated PES in Figure S1.

[2]Calculated HOMO–LUMO gap for the corresponding neutral isomers of **b** and **c** based on simulated PES in Figure S1.

[3]Isomer **d** of Ge_{15}^- is 0.97eV higher relative to isomer **a**, displayed in Figure S1.

Table S3. Calculated vertical detachment energy (VDE) for Ge_n^- ($3 \leq n \leq 20$) shown in Figure 1.

Anions	VDE (calcd.)
Ge_3^-	2.38[b](*s*-2.50, *t*-2.25)[a]
Ge_4^-	*s*-1.99
Ge_5^-	*s*-2.84
Ge_6^-	*s*-2.20
Ge_7^-	*s*-2.13
Ge_8^-	2.90(*s*-2.72, *t*-3.08)
Ge_9^-	3.56(*s*-3.49, *t*-3.62)
Ge_{10}^-	*s*-3.31
Ge_{11}^-	2.74(*s*-2.34, *t*-3.13)
Ge_{12}^-	2.90(*s*-2.67, *t*-3.12)
Ge_{13}^-	*s*-3.59
Ge_{14}^-	*s*-3.19
Ge_{15}^-	*s*-3.25
Ge_{16}^-	3.08(*s*-2.76, *t*-3.40)
Ge_{17}^-	3.15(*s*-2.78, *t*-3.51)
Ge_{18}^-	*s*-2.78
Ge_{19}^-	3.19(*s*-2.88, *t*-3.50)
Ge_{20}^-	3.46(*s*-3.19, *t*-3.72)

[a]The prefix *s*- and *d*- denote VDEs arising from the transitions to singlet and triplet state of neutral, respectively. [b]Arithmetic mean of *s*- and *d*-VDE assuming the weight of either transition to the observed VDE is equal.

References

1. Y. Negishi, H. Kawamata, F. Hayakawa, A. Nakajima and K. Kaya, *Chem. Phys. Lett.*, 1998, **294**, 370-376.
2. O. Cheshnovsky, S. H. Yang, C. L. Pettiette, M. J. Craycraft, Y. Liu and R. E. Smalley, *Chem. Phys. Lett.*, 1987, **138**, 119-124.