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Anion photoelectron spectroscopy and quantum chemistry calculations of $TaSi_{16}^{-/0}$ clusters: Global minimum fullerene-like cage structures, bonding and superatom properties

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The Jellium model

The idea of stable clusters as building blocks was proposed by Khanna and Jena. These unique clusters would interact weakly instead of coalescing. At the time there was one cluster class that showed extreme promise in this endeavor; jellium -magic metallic cluster. Magic metallic clusters were first observed by Knight and co-workers. They noticed when the number of sodium atoms in a cluster were 2. 8. 18, 20, etc, these particular clusters were more abundant. These magic numbers were interpreted as reflecting an electronic shell structure, much like in atoms or nuclei in nucleons as predicted by Ekardt. Knight, Clemenger and co-workers developed an empirical jellium model based on quantum mechanics from the boundary conditions imposed by a potential. The empirical jellium model is based on single particle potentials and solving the one-electron Schrodinger equation for a particle inside a sphere.

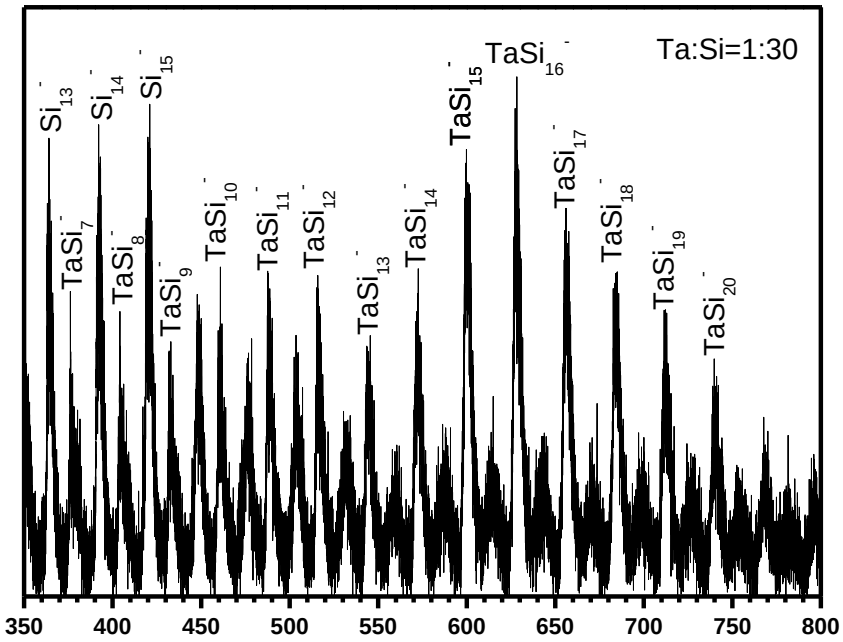

Figure S1. Mass Spectrum at sample mole ratio 1:30.

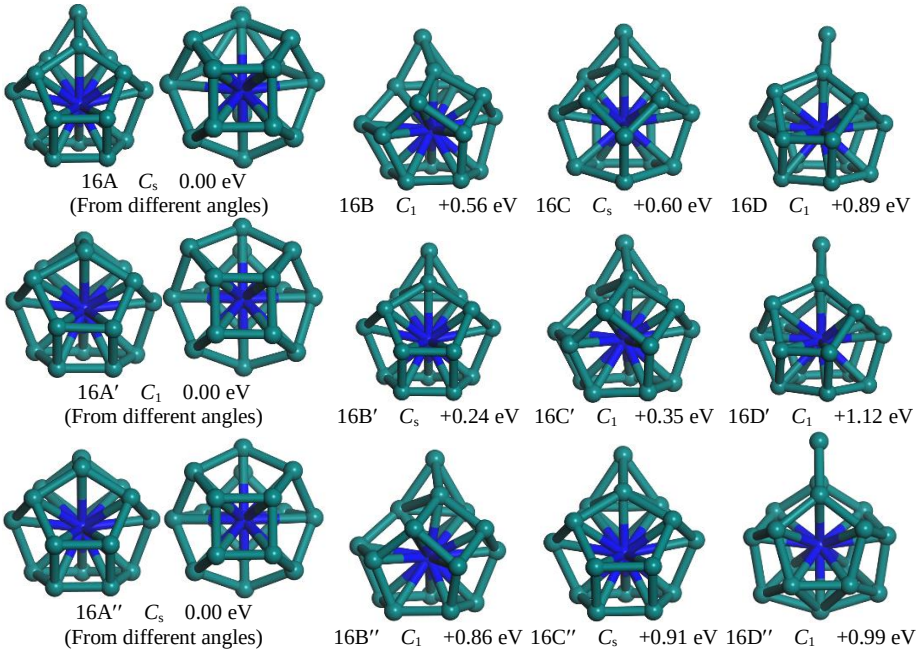

Figure S2. Low-lying isomers of $TaSi_{16}^{-/0/+}$ clusters. The front and side views of the global minima are given. The relative energies are obtained at CCSD(T) level. The green and blue balls stand for the Si atoms and Ta atoms, respectively.

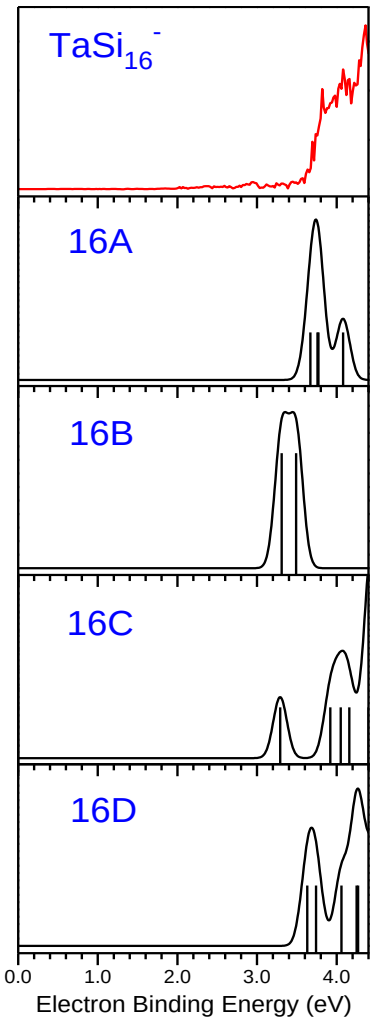

Figure S3. Photoelectron spectrum of $TaSi_{16}^-$ cluster recorded with 266 nm photons and comparison with the DOS spectra of low-lying isomers at the B3LYP level. The simulated spectra were obtained by fitting the distribution of the transition lines with unit-area Gaussian functions of 0.15 eV full width at half maximum (FWHM). The vertical lines are the theoretical simulated spectral lines of $TaSi_{16}^-$ cluster.

Table S1. Relative energies, theoretical VDEs and ADEs of the low-lying isomers of $TaSi_{16}^-$, along with the experimental VDEs and ADEs. The isomers labeled in bold are the most probable isomers in the experiments.

Isomers		Electronic state	ΔE[a] (eV)	VDE (eV)		ADE (eV)	
				Theo.[b]	Expt.[c]	Theo.[b]	Expt.[c]
$TaSi_{16}^-$	**16A**	$^1A'$	0.00	3.68	3.81	3.54	3.60
	16B	^1A	0.56	3.31		3.16	
	16C	$^1A'$	0.60	3.29		3.08	
	16D	^1A	0.89	3.63		3.50	

[a] The relative energies are calculated at the CCSD(T) level.
[b] The ADEs and VDEs are calculated at the B3LYP level.
[c] The experimental uncertainties of the VDEs and ADEs are ±0.08 eV.

Table S2. Cartesian coordinates of the low-lying isomers of $TaSi_{16}^-$.

$TaSi_{16}^-$

	16A				16B		
	X	Y	Z		X	Y	Z
Si	-2.75510000	0.00000000	0.45900000	Si	2.01310000	-1.20830000	-1.67780000
Si	0.00000000	1.24930000	2.64630000	Si	-0.21330000	-1.92790000	-1.90630000
Si	1.71180000	1.94730000	1.16430000	Si	-0.67030000	-2.92480000	0.18880000
Si	2.75510000	0.00000000	0.45900000	Si	-2.43660000	-1.51310000	-0.17680000
Si	-1.20490000	2.08830000	-1.20340000	Si	-1.78390000	0.02990000	-2.21650000
Si	1.71180000	-1.94730000	1.16430000	Si	2.04500000	1.16820000	-1.67080000
Si	1.20490000	2.08830000	-1.20340000	Si	2.53890000	-1.18730000	0.62070000
Si	1.20490000	-2.08830000	-1.20340000	Si	2.56570000	1.12050000	0.62780000
Si	-1.71180000	-1.94730000	1.16430000	Si	-0.60180000	2.93880000	0.19980000
Si	2.33200000	0.00000000	-1.96890000	Si	-2.26410000	0.02200000	1.55920000
Si	-2.33200000	0.00000000	-1.96890000	Si	0.74760000	1.88880000	1.87550000
Si	-1.20490000	-2.08830000	-1.20340000	Si	-0.30150000	-0.00150000	2.78210000
Si	-1.71180000	1.94730000	1.16430000	Si	-0.16230000	1.94250000	-1.89850000
Ta	0.00000000	0.00000000	0.09340000	Si	0.70220000	-1.91220000	1.86700000
Si	0.00000000	-1.24930000	2.64630000	Ta	0.04220000	-0.00050000	-0.00050000
Si	0.00000000	0.00000000	-2.72540000	Si	-2.39870000	1.56680000	-0.17130000

	16C				16D		
	X	Y	Z		X	Y	Z
Si	-0.11160000	-0.16310000	2.84840000	Si	-0.52410000	-2.73290000	-0.02090000
Si	0.51010000	-2.03090000	1.57470000	Si	-1.81450000	-1.43530000	1.40160000
Si	0.51010000	-2.03090000	-1.57470000	Si	-0.51100000	-1.95840000	-2.28460000
Si	-0.11160000	-0.16310000	-2.84840000	Si	2.51040000	1.16000000	0.97560000
Si	-1.85840000	1.04620000	-1.83170000	Si	2.29200000	0.76310000	-1.31600000
Si	-1.85840000	1.04620000	1.83170000	Si	-1.23010000	1.96450000	1.38590000
Si	1.66180000	1.45450000	2.26370000	Si	0.82110000	2.63960000	0.41360000
Si	2.36740000	-0.55710000	1.17700000	Si	-3.05440000	0.31840000	0.42600000
Si	2.36740000	-0.55710000	-1.17700000	Si	-2.18070000	-0.36170000	-1.69550000
Si	1.66180000	1.45450000	-2.26370000	Si	0.61640000	2.31310000	-1.98250000
Si	-0.17580000	2.62270000	-1.17610000	Si	-1.64760000	1.90090000	-1.21420000
Si	-0.17580000	2.62270000	1.17610000	Si	1.76010000	-1.46670000	-1.61140000
Si	-2.91510000	-0.07840000	0.00000000	Ta	0.05020000	-0.03270000	-0.00250000
Si	-0.39720000	-3.89480000	0.00000000	Si	1.60020000	-0.63030000	2.21990000
Si	-1.50270000	-1.88920000	0.00000000	Si	1.68240000	-2.34120000	0.59040000
Ta	0.00560000	0.21200000	0.00000000	Si	-0.58190000	0.03710000	2.72550000

Table S3. Cartesian coordinates of the low-lying isomers of $TaSi_{16}$.

$TaSi_{16}$

	16A′				16B′		
	X	Y	Z		X	Y	Z
Si	-2.75510000	0.00000000	0.45900000	Si	2.01310000	-1.20830000	-1.67780000
Si	0.00000000	1.24930000	2.64630000	Si	-0.21330000	-1.92790000	-1.90630000
Si	1.71180000	1.94730000	1.16430000	Si	-0.67030000	-2.92480000	0.18880000
Si	2.75510000	0.00000000	0.45900000	Si	-2.43660000	-1.51310000	-0.17680000
Si	-1.20490000	2.08830000	-1.20340000	Si	-1.78390000	0.02990000	-2.21650000
Si	1.71180000	-1.94730000	1.16430000	Si	2.04500000	1.16820000	-1.67080000
Si	1.20490000	2.08830000	-1.20340000	Si	2.53890000	-1.18730000	0.62070000
Si	1.20490000	-2.08830000	-1.20340000	Si	2.56570000	1.12050000	0.62780000
Si	-1.71180000	-1.94730000	1.16430000	Si	-0.60180000	2.93880000	0.19980000
Si	2.33200000	0.00000000	-1.96890000	Si	-2.26410000	0.02200000	1.55920000
Si	-2.33200000	0.00000000	-1.96890000	Si	0.74760000	1.88880000	1.87550000
Si	-1.20490000	-2.08830000	-1.20340000	Si	-0.30150000	-0.00150000	2.78210000
Si	-1.71180000	1.94730000	1.16430000	Si	-0.16230000	1.94250000	-1.89850000
Ta	0.00000000	0.00000000	0.09340000	Si	0.70220000	-1.91220000	1.86700000
Si	0.00000000	-1.24930000	2.64630000	Ta	0.04220000	-0.00050000	-0.00050000
Si	0.00000000	0.00000000	-2.72540000	Si	-2.39870000	1.56680000	-0.17130000

	16C′				16D′		
	X	Y	Z		X	Y	Z
Si	-0.11160000	-0.16310000	2.84840000	Si	-0.52410000	-2.73290000	-0.02090000
Si	0.51010000	-2.03090000	1.57470000	Si	-1.81450000	-1.43530000	1.40160000
Si	0.51010000	-2.03090000	-1.57470000	Si	-0.51100000	-1.95840000	-2.28460000
Si	-0.11160000	-0.16310000	-2.84840000	Si	2.51040000	1.16000000	0.97560000
Si	-1.85840000	1.04620000	-1.83170000	Si	2.29200000	0.76310000	-1.31600000
Si	-1.85840000	1.04620000	1.83170000	Si	-1.23010000	1.96450000	1.38590000
Si	1.66180000	1.45450000	2.26370000	Si	0.82110000	2.63960000	0.41360000
Si	2.36740000	-0.55710000	1.17700000	Si	-3.05440000	0.31840000	0.42600000
Si	2.36740000	-0.55710000	-1.17700000	Si	-2.18070000	-0.36170000	-1.69550000
Si	1.66180000	1.45450000	-2.26370000	Si	0.61640000	2.31310000	-1.98250000
Si	-0.17580000	2.62270000	-1.17610000	Si	-1.64760000	1.90090000	-1.21420000
Si	-0.17580000	2.62270000	1.17610000	Si	1.76010000	-1.46670000	-1.61140000
Si	-2.91510000	-0.07840000	0.00000000	Ta	0.05020000	-0.03270000	-0.00250000
Si	-0.39720000	-3.89480000	0.00000000	Si	1.60020000	-0.63030000	2.21990000
Si	-1.50270000	-1.88920000	0.00000000	Si	1.68240000	-2.34120000	0.59040000
Ta	0.00560000	0.21200000	0.00000000	Si	-0.58190000	0.03710000	2.72550000