Structural and Electronic Properties of Metal-Encapsulated Silicon Clusters in a Large Size Range

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[1]*Department of Theoretical Studies, Institute for Molecular Science, Okazaki 444-8585, Japan*
[2]*Mesoscopic Physics Laboratory, Department of Physics, Peking University, Beijing 100871, People's Republic of China*

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- MSi_n (M = W, , O , P , C , .) $3 \le n \le 20$ *ab initio* . D MSi_n, w Si_n . Tw . T $M@Si_n$ - $10 \le n \le 16$. T w fi .

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T - fi w w . - - . H w , - 1 (DB) 2 4 - . T w - Si_n . A (SiH_4) w M^+ (M = Hf, T , , , I , .) MSi_nH_x ($x \le 4$ n). E MSi_n n = 14, 13, 12, 11, 9, - , . T MSi_nH_x M . T , M Si_n 5 , *ab initio* fi w WSi_{12}. T MSi_n . (1) I w Si_n - ? (2) MSi_n ? (3) MSi_n w fi 5 ? A , w *ab initio* - - MSi_ns (M = W, , O , P , C , .) ($3 \le n \le 20$). T w - w B3L Y P (B - L - Y -P) - 6 . P , L L2D LanL2DZ(d), M , - . T -

7 . I , - , 6-311 + $G(d)$, MSi_n , - Os@Si_{14}. T Si_n MSi_n - T I. T w M . H , w fi - fi . T (EE) M Si_n fi EE = $E[Si_n] + E[M] - E[MSi_n]$, $E[Si_n]$ Si_n 3,4 . T K - w (HOMO) w (L MO) BL Y P w 9 11 . A M- Si_n fi : M (. .,), DB , HOMO-L MO 0.50 11,12 . T M- - fi 2.93 2.70 Å, . T w M- Si_n - w 5 T II. T w - Si_n F . 1, M- Si_n 5 $M \neq$ 6 F . 2. A fi , , WSi_3, $PtSi_3$, $CoSi_9$, . T WSi_3 DB H, w

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TABLE I. Si_n MSi_n . Tw $M@Si_{1s}$: w $M@Si_{16}$ w $M@Si_{20}$. *tri*: ; *tetra*: ; *p*: ; *b*: ; *h*: ; *c*: ; *d*: ; *f*: ; *hp*: ; *FK*: F -K .

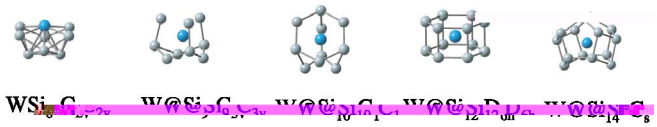
	I
Si_s 8	D_{3d} , C_{2v} C_{3v} , C_{2v} *tri* , D_{4h} *tetra* , D_{4d} *tetra*
Si_9 8	C_{3v} , D_{3h} *tri*
Si_{10} 8	D_{5h} *p* , D_{5d} *p* , T_d , C_{3v} *tri* , D_{4d} *tetra*
Si_{12} 3,5	*b* , C_{2v} *tri* D_{6h} *h* , D_{6d} *h* , I_h
Si_{14} 9	*c*, *d*, *f* , D_{7h} *hp* , D_{6h} *h*
Si_{15} 10	*f*, *c*1, *c*2
Si_{16} 9	*f* *FK* , *h*
Si_{20}	I_h

w . A - WSi_n WSi_nH_x $n = s$ (30%) 5 . T w w - T - Si_n 13 , WSi_n $W@Si_n$ $\Delta E = E_{exo} - E_{endo} =$ $W@Si_n$ w $W@Si_{10}$, -0.50, 0.39, 1.63, ≈ 6 eV (- . H , D_{6h}) $n = s$, 9, 10, 12, , $n = 12$, w . T $M@Si_n$ - w $n = 10$ $n = 16$. T - . T *M*- $M@Si_n$ $Os@Si_{10}$, w C_{3v} w O - -

TABLE II. T (NDB_{theor}) (NDB_{expt}) 5 DB , HOMO-L MO ( ), , EE ( ), BE (, eV/), *M* *M*- Si_n . T *L* *H* w , . $Fe@Si_{10}$ $2\mu_B$ w . A $Pt@Si_n$ - $M@Si_n$ ($n = 17$ 10 , 18, 20) w DB .

M- Si_n	NDB_{theor}	NDB_{expt}	G	C	EE	BE	C
WSi_s	0	0	0.95	*L*	5.43	3.44	-0.41
$PtSi_s$	11	···	1.38	*L*	4.35	3.33	-0.10
$W@Si_9$	9		1.19	*L*	5.14	3.42	-2.14
$CoSi_9$	1	0	0.34	*L*	3.96	3.12	0.49
$W@Si_{10}$	6		1.39	*L*	5.09	3.50	-1.74
$Os@Si_{10}$	0	···	1.48	*H*	5.60	3.55	-1.19
$Ru@Si_{10}$	2	···	0.72	*L*	4.21	3.42	-1.26
$Fe@Si_{10}$	0	···	0.25	*L*	2.27	3.25	$-0.s0$
$W@Si_{12}$	0	0	1.38	*H*	8.64	3.69	-1.74
$Zr@Si_{12}$ (C_1)	8		0.78	*L*	4.81	3.40	-0.45
$Os@Si_{12}$ (D_{6h})	0	···	1.10	*H*	8.36	3.67	$-1.2s$
$W@Si_{14}$ (*f*)	0	···	0.38	*L*	8.74	3.70	$-1.9s$
$Zr@Si_{14}$ (*dbhpa*)	1	0	0.65	*L*	6.34	3.54	-1.97
$Zr@Si_{14}$ (*dbhpb*)	0	0	1.23	*H*	6.18	3.53	-2.13
$Os@Si_{14}$ (*c*)	0	···	1.63	*H*	7.19	3.60	$-1.6s$
$W@Si_{15}$ (*f*)	0	···	0.79	*H*	10.06	3.71	-2.04
$W@Si_{16}$ (*f*)	1	···	1.11	*L*	10.22	3.73	-2.13
$Zr@Si_{16}$ (*f*)	0	···	1.52	*H*	9.59	3.69	-2.19
$W_2@Si_{20}$	0	···	0.55	*H*	16.75	3.65	-1.95

O 6-311 + *G*(*d*) , w LanL2DZ(*d*) *dbhpa* .



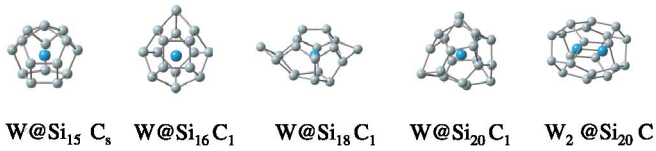


FIG. 1 ( ). G - Si_n $W_2@Si_{20}$. T .
F ,
. T $Mo@Si_{12}$
$Cr@Si_{12}$ w $W@Si_{12}$. T $Os@Si_{15}$
$Zr@Si_{16}$ *f* , w $Pt@Si_{14}$,
$M@Si_{15}$ (*M* =

2.39 2.49 Å 2.36 2.43 Å, . T w
$Zr@Si_{14}$ C_1
(*dbhpa*) ,
d w .
H w , DB

H $Zr@Si_{14}$ 5 . D_{6h}
h , D_{2h} -
(*dbhpb*) w w w -
. I 0.16
dbhpa , DB . K
w
-
5,13,14 , w
15 . T
. 16 . T w , 1200 K,
dbhpb
dbhpa . T - -
2.72 2.93 Å 2.23 2.42 Å, ,
dbhpb .

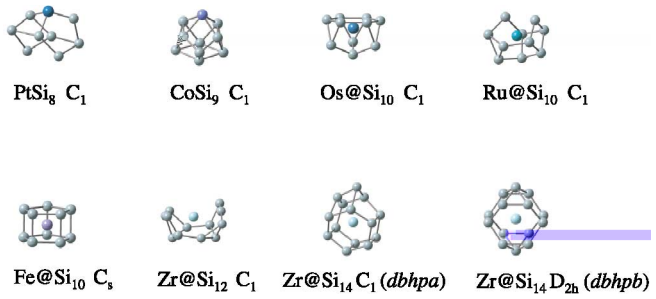


FIG. 2 ( ). G *M*- Si_n
$M \neq$ 6
w $Zr@Si_{12}$

T w
O $Os@Si_{10}$
F . 3( ) w w , w
w O

F . 3( ) . I $Zr@Si_{14}$,
- , w
F . 3( ). F T II,
−2 −1 O ,
. H , w O
Si_{10} , ,
, w w
Si_{14} w . C -
, w O ( )
Si_{10} (Si_{14}) , fi
EE O (5.60) (6.18)
Si_{10} Si_{14}, .
F 4 w EE
BE *M*- Si_n (*M* = W, , O , P).
I , BE w -
, $n = 16$. B
$n = 16$,
$n =$ 12 *M* = W, $n = 14$ *M* = Zr P ,
$n = 12$ *M* = Os. I *M* ,
, . ., $n = 16$,
(*M* = W,
$n = 15$ BE
$n = 16$). H w , ,
w w -
. C w -
10,17 , fi
fi w
$n = 12$ 5 $n = 15$ 16 14
- Si_n w
, -
. T w $n = 14$
- Si_n
w
w . T EE-*n* BE-*n*
. I , EE w
w *M*- ,

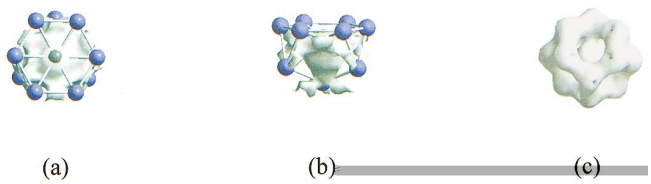


FIG. 3 ( ). C
( ) $Os@Si_{10}$ w ,
( ) ( ) w ,
( ) *dbhpb* $Zr@Si_{14}$. T
0.060 0.045 . . $Os@Si_{10}$ $Zr@Si_{14}$,
.

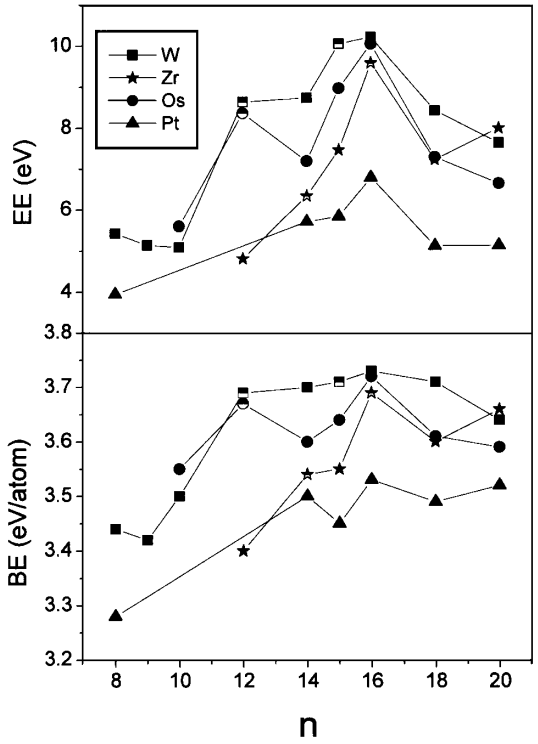


FIG. 4. EE BE *M*-Si$_n$ w M = W, , O , P . T w -fi .

n = 16 w . T M w 16, w M@Si$_n$. T Si$_n$, . O Si$_{20}$ (F . 1). , BE-n EE-n Zr@Si$_{14}$, w M Si$_n$. N fi w , W@Si$_{12}$, W@Si$_{15}$, Zr@Si$_{14}$, Zr@Si$_{16}$, Os@Si$_{12}$. I , w Si$_n$, Si$_n$. Tw M@Si$_n$s (Os@Si$_{10}$ Zr@Si$_{14}$) fi , M@Si$_n$ - - 10 ≤ n ≤ 16. T

W@Si$_{12}$, W@Si$_{15}$, Zr@Si$_{14}$, Zr@Si$_{16}$, Os@Si$_{12}$, w w w w n = 12 14 - - , 5 .

A w GA IAN 98 18 . T w w J P , N FC (G N . 10104001), T A . P . K W@Si$_{15}$ S. , S. C , . , N. T , . , S. .

*E : @ . .
E : @ . .

1 F , M. F. J J. E. B w , J. C . P . **96**, 9180 (1992), .
2 . , . A , M. P , P . . L . **72**, 665 (1994).
3 K. M. H *et al.*, N (L) **392**, 582 (1998).
4 I. *et al.*, P . . L . **85**, 546 (2000).
5 H. H , T. M , T. K , P . . L . **86**, 1733 (2001).
6 A. D. B , J. C . P . **98**, 5648 (1993).
7 P. J. H . . , J. C . P . **82**, 270 (1985); **82**, 299 (1985); . . P. J. H , *ibid.* **82** , 284 (1985).
8 K. C. M. fi , J. C . P . **89**, 2219 (1988).
9 . K S. K w , P . . L . **87**, 045503 (2001).
10 . K S. K w , P . . B **65**, 073404 (2001).
11 B. L. *et al.*, J. C . P . **98**, 3095 (1993).
12 F. D *et al.*, **252**, 548 (1991).
13 M. *et al.*, T . M . . . J . **25**, 1003 (2000); M. O *et al.*, J. P . C . A **106**, 3702 (2002).
14 . M. B , J. C . P . **87**, 4233 (1987); **90**, 6306 (1989).
15 J. M. L. M , J. EI-S , J.-P. F , C . P . L . **248**, 345 (1996).
16 D. A. M , *Statistical Thermodynamics* (H & w, N w S , 1973).
17 . N. K , B. K. , P. J , P . . L . **89**, 016803 (2002).
18 M. J. F *et al.*, *Gaussian 98 Revision A.9* (G , I ., P , PA, 1998).