

On the electron affinity of SiN and spectroscopic constants of SiN⁻

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Accurate spectroscopic constants and energetics were calculated for the two lowest-lying states of SiN and SiN⁻ employing the coupled cluster methodology and very large basis sets (up to doubly augmented sextuple- ζ quality) accounting also for core/valence correlation, one-electron Douglas-Kroll-Hess relativistic effects, and atomic spin-orbit couplings. Our best estimate for the adiabatic electron affinity of SiN is 3.002 eV, in very good agreement with the recent, experimentally determined value of 2.949(8) eV. However, the calculated bond length of the SiN⁻ $X^1\Sigma^+$ state at the same level, $r_e=1.5904$ Å, is smaller than the indirectly extracted experimental value of 1.604(5) Å, pointing out that the latter value is either a bit overestimated or not as accurate as the ± 0.005 Å error bar indicates. For the neutral SiN, all calculated data are in excellent agreement with previous accurate experimental results. © 2005 American Institute of Physics. [DOI: 10.1063/1.2035591]

I. INTRODUCTION

Recently, Meloni *et al.*¹ recorded the negative-ion photoelectron spectra of SiN⁻ using 355- and 266-nm photodetachment wavelengths. The measured spectra probed the transitions from the $X^1\Sigma^+$ ground state of SiN⁻ to the $X^2\Sigma^+$ and $A^2\Pi$ states of SiN. Notwithstanding the similarity with the isovalent cyanoradical (CN) and its anion (CN⁻), it is perhaps rather surprising that this was the first time ever that spectroscopic constants of SiN⁻ and the electron affinity (EA) of SiN were measured experimentally. Established experimental data for SiN and Si were used in order to determine corresponding values for SiN⁻. In particular, bond lengths of the $X^2\Sigma^+$ and $A^2\Pi$ states of SiN were taken from the highly accurate work of Hirota and co-workers, $r_e=1.572\,066\pm 0.000\,041$ (Ref. 2) and $1.641\,879\pm 0.000\,020$ Å,³ respectively. The bond dissociation energy of SiN with respect to the asymptotic Si(³P)+N(⁴S) fragments was taken from the work of Naulin *et al.*,⁴ $D_0=4.68\pm 0.14$ eV or 107.9 ± 3.2 kcal/mol, while the EA of Si used was the value measured by Blondel *et al.*,⁵ EA(Si)=1.3895 eV. Combining the above data with their own measurements, Meloni *et al.* obtained $r_e(\text{SiN}^-)=1.604\pm 0.005$ Å, $\omega_e(\text{SiN}^-)=1130\pm 20$ cm⁻¹, EA(SiN)=2.949 \pm 0.008 eV, and from that, $D_0(\text{SiN}^-)=D_0(\text{SiN})+\text{EA}(\text{SiN})-\text{EA}(\text{Si})=6.24\pm 0.15$ eV (143.9 \pm 3.4 kcal/mol).¹

Although the spectroscopic parameters of SiN⁻ appear to be in fairly good agreement with the theoretical values of Kalcher calculated at the multireference-averaged coupled-pair functional (MRACPF) level in conjunction with Dunning's correlation-consistent polarized valence quadruple- ζ (cc-pVQZ) basis set ($r_e=1.6045$ Å and $\omega_e=1120$ cm⁻¹),⁶ the electron affinity was predicted to be smaller by about 0.1 eV (EA=2.862 eV). An older calculation of Peterson and

Woods⁷ using the Møller-Plesset perturbation theory including single, double, and quadruple terms in the expansion (MP4SDQ/ \sim QZ+P) predicted a smaller SiN⁻ bond length ($r_e=1.5940$ Å) but much higher electron affinity (EA=3.33 eV). Finally, McLean *et al.* have calculated $r_e=1.573$ and 1.586 Å at the singles and doubles configuration-interaction (CISD) and CISD+Davidson correction (CISD+Q) levels of theory using Slater-type orbitals.⁸

Given the academic importance of SiN⁻ as an isovalent to CN⁻ species, the practical importance of its being a molecular subunit to the silicon nitride compound (Si₃N₄) which has considerably interesting properties as an engineering material,⁹ as well as the aforementioned experimental results and the availability of large basis sets including "tight" basis functions suitable to describe the $2s^22p^6$ semicore/valence correlation of Si,¹⁰ we performed high-level basis-set-extrapolated theoretical calculations with the purpose of obtaining results on the spectroscopic constants and dissociation energies for the two lowest-lying states of SiN and SiN⁻.

II. TECHNICAL DETAILS

We have employed the (restricted) coupled cluster method including single and double excitations, along with a noniterative estimate of the connected triple excitations, based on a restricted Hartree-Fock reference wave function (RHF-RCCSD(T)).¹¹ The correlation-consistent basis sets of Dunning and co-workers were employed.^{10,12} Five families of these sets were used; first, the plain cc-pVnZ series was engaged, augmented with diffuse functions on both atoms, and denoted aug-cc-pVnZ,^{12(a)-12(c)} $n=3-6$. The same series was also used but with the addition of a tight d function on Si, as suggested by Dunning *et al.* for smoother extrapolation, and denoted aug-cc-pV(n+d)Z,^{12(f)} $n=3-6$. The third and fourth families employed the latter basis set including

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either a second shell of diffuse functions on N,^{12(g)} and denoted d-aug-cc-pV($n+d$)Z, $n=3-6$, or a “weighted core” (wC) set of tight functions for Si,¹⁰ suitable for describing the correlation of the inner $2s^2 2p^6$ shell of Si. This set will be referred to as aug-cc-pwCV($n+d$)Z, but with $n=3-5$, since no wC basis set of sextuple- ζ quality is available for Si. Finally, the fifth basis set family included the aug-cc-pVnZ series in which the nonaugmented part has been recontracted to account for one-electron relativistic Douglas-Kroll-Hess effects and designated as aug-cc-pVnZ-DKH, $n=2-5$.^{12(h)} The largest basis set used in the present work, d-aug-cc-pV(6+d)Z: (22s15p7d5f4g3h2i_{Si}/18s12p7d6f5g4h2i_N) \rightarrow [9s8p7d5f4g3h2i_{Si}/9s8p7d6f5g4h2i_N] numbers 423, generally contracted spherical Gaussian functions.

The results obtained were extrapolated to the “complete basis set” (CBS) limit with the mixed exponential/Gaussian formula¹³

$$P_n = P_\infty + A e^{-(n-1)} + B e^{-(n-1)^2},$$

where P is a generic property, P_∞ its CBS limit, n the cardinal basis-set number, while A and B are freely adjustable parameters. Since not all cardinal numbers $n=2-6$ are available for all the families of basis sets used, there is more than one way to compare extrapolated results. For example, with the core/valence sets, only a three-point TQ5 extrapolation is possible with the formula (1); however, with the aug-cc-pVnZ series, one can perform TQ5, Q56, or even TQ56 extrapolations. In principle, significant differences between the extrapolated values among the different extrapolating schemes are not expected, and indeed, only slight differences are observed. However, in order to be consistent when we compare extrapolated values, we will compare at the same extrapolated level, preferably Q56 if available. Taking that into account, the procedure we will generally use in the present work to obtain “best estimates” is as follows: (a) first, we obtain the Q56-extrapolated RCCSD(T)/d-aug-cc-pVnZ result and to this we add (b) the core/valence effect, Δ_{CV} , of the $2s^2 2p^6$ core of Si, defined as the difference in the CBS(TQ5) values between the aug-cc-pV($n+d$)Z and aug-cc-pwCV($n+d$)Z sets, (c) the scalar relativistic effect, Δ_{DKH} , defined similarly as the difference in extrapolated CBS(TQ5) values between the aug-cc-pVnZ and aug-cc-pVnZ-DKH sets, and (d) an atomic Si(3P) spin-orbit correction for the binding energies only, Δ_{SO} , taken from the experiment.^{14,15} Note that the procedure followed resembles the well-established way of Dixon, Feller, and Peterson of obtaining accurate thermochemical values for enthalpies of formation for small molecules.¹⁶

All calculations were performed with the MOLPRO 2002.6 software package.¹⁷

III. RESULTS AND DISCUSSION

Table I presents the total energies of the Si, Si⁻, and N fragments in their ground states as well as the calculated electron affinity of Si. Note that the highly accurate experimental EA(Si) value of Blondel *et al.*,⁵ 1.389 522 0 \pm 0.000 002 4 eV, refers to the Si(3P_0) \leftarrow Si(4S) transition. Our Q56-extrapolated theoretical value at the

RCCSD(T)/aug-cc-pV($n+d$)Z level of theory is 1.4097 eV, which after correcting for the $2s^2 2p^6$ Si core/valence correlation, DKH relativistic effects and the experimental spin-orbit coupling using the $^3P_1 \leftarrow ^3P_0$ and $^3P_2 \leftarrow ^3P_1$ splittings of 77.111 867(24) and 146.045 302(7) cm⁻¹, respectively,^{14,15} becomes 1.3736 eV, differing only 128 cm⁻¹ from the experiment.

Results for the $X^2\Sigma^+$ and $A^2\Pi$ states of SiN are collected in Table II, while Table III contains similar results for the $X^1\Sigma^+$ and $a^3\Sigma^+$ states of SiN⁻ in order of increasing quality.

As seen in Table II, the value of the calculated extrapolated nonrelativistic electron affinity of SiN shows no dependence on the family of basis sets used. Only scalar relativity reduces the EA by about 0.010 eV. Our calculated harmonic vibrational constants ω_e for SiN($X^2\Sigma^+$) and SiN⁻($X^1\Sigma^+$) are 1155.5 and 1141.6 cm⁻¹ at the RCCSD(T)/aug-cc-pwCV(5+d)Z level of theory, in agreement with the experimental values of 1151.30(11) and 1130(20) cm⁻¹, respectively.^{21,1} Our best adiabatic EA results with respect to potential-energy minima and to zero-point vibrational levels are 3.001 and 3.002 eV, respectively, in agreement with the experimental value of Meloni *et al.*, EA=2.949 \pm 0.008 eV.¹ Taking into account the similar agreement with the EA of Si, it comes as no surprise that the best estimated binding energies of ground-state SiN (106.7 kcal/mol) and SiN⁻ (144.3 kcal/mol) are in agreement with the experimental values 109.6 \pm 3.2 and 145.5 \pm 3.4 kcal/mol, respectively. The contribution of the $2s^2 2p^6$ core electrons of Si to the binding energy of the ground states is 1.0 (SiN) and 1.2 (SiN⁻) kcal/mol, while scalar relativistic effects reduce D_e by a constant value of 0.2 kcal/mol in all four states studied. Note that there is no first-order atomic spin-orbit correction in SiN⁻ because the dissociation products, Si(4S) + N(4S), are both in S states.

The bond length of SiN⁻($X^1\Sigma^+$) was experimentally found to be $r_e = 1.604 \pm 0.005$ Å.¹ This value was obtained by simulating the observed photoelectronic spectrum within the Franck-Condon approximation, utilizing established spectroscopic data (r_e , ω_e , and $\omega_e x_e$) for the $X^2\Sigma^+$ and $A^2\Pi$ states of SiN. Our extrapolated bond length for SiN⁻($X^1\Sigma^+$) at the RCCSD(T)/d-aug-cc-pV($n+d$)Z level of theory is 1.5963 Å, showing practical independence of the extrapolation scheme, while upon inclusion of the $2s^2 2p^6$ core correlation of Si and Douglas-Kroll-Hess relativistic effects, the bond distance gets even shorter by 0.0055 and 0.0004 Å, thus the best estimated value obtained is $r_e = 1.5904$ Å. This result indicates that the experimental bond length could have either been overestimated by about 0.01 Å, or that the ± 0.005 error is, in fact, larger. In order to examine this hypothesis, we calculated the bond lengths of the $X^2\Sigma^+$ and $A^2\Pi$ states of SiN and contrasted them with the highly accurate values of the literature that Meloni *et al.* used in calculating the r_e for SiN⁻($X^1\Sigma^+$). Indeed, our “best” r_e values for both the $X^2\Sigma^+$ and $A^2\Pi$ states at the extrapolated RCCSD(T)/d-aug-cc-pV($n+d$)Z + Δ_{CV} + Δ_{DKH} level of theory, 1.5713 and 1.6394 Å, respectively, are in excellent agreement with the accurate values of Hirota and co-workers, 1.572 066(41) and 1.641 879(20) Å;^{2,3} see Table II. Therefore, we believe that

TABLE I. Total energies (E_h) of the ground states of Si, Si⁻ and N, and electron affinity EA (eV) of Si, at the RCCSD(T) level of theory.

Basis set	Si(³ P)	Si ⁻ (⁴ S)	EA(Si)	N(⁴ S)
aug-cc-pVTZ	-288.933 548	-288.984 448	1.3851	-54.516 521
aug-cc-pVQZ	-288.937 529	-288.989 034	1.4015	-54.525 095
aug-cc-pV5Z	-288.938 799	-288.990 490	1.4066	-54.527 798
aug-cc-pV6Z	-288.939 249	-288.991 014	1.4086	-54.528 650
CBS(TQ56)			1.4097(1)	
CBS(TQ5)			1.4110	
CBS(Q56)			1.4096	
aug-cc-pVTZ-DKH	-289.536 784	-289.587 411	1.3776	-54.545 782
aug-cc-pVQZ-DKH	-289.540 980	-289.592 209	1.3940	-54.554 429
aug-cc-pV5Z-DKH	-289.542 321	-289.593 736	1.3991	-54.557 153
CBS(TQ5)			1.4036	
aug-cc-pV(T+d)Z	-288.933 860	-288.984 737	1.3844	
aug-cc-pV(Q+d)Z	-288.937 727	-288.989 231	1.4015	
aug-cc-pV(5+d)Z	-288.938 892	-288.990 589	1.4067	
aug-cc-pV(6+d)Z	-288.939 287	-288.991 056	1.4087	
CBS(TQ56)			1.4098(1)	
CBS(TQ5)			1.4114	
CBS(Q56)			1.4097	
d-aug-cc-pVTZ				-54.516 592
d-aug-cc-pVQZ				-54.525 127
d-aug-cc-pV5Z				-54.527 818
d-aug-cc-pV6Z				-54.528 657
aug-cc-pwCV(T+d)Z	-289.197 423	-289.247 925	1.3742	
aug-cc-pwCV(Q+d)Z	-289.245 297	-289.296 427	1.3913	
aug-cc-pwCV(5+d)Z	-289.264 486	-289.315 827	1.3971	
CBS(TQ5)			1.4013	
Δ_{CV}^a			-0.0101	
Δ_{DKH}^b			-0.0074	
Δ_{SO}^c			-0.0186	
Best estimate ^d			1.3736	
Expt. ^e			1.389 522 0(24)	

^aCore/valence effect.^bOne-electron Douglas-Kroll-Hess relativistic effect.^cSpin-orbit correction value obtained by using the experimental $^3P_1 \leftarrow ^3P_1$ and $^3P_2 \leftarrow ^3P_1$ spin-orbit splittings, Refs. 14 and 15.^dSee text for details.^eExperimental value refers to the $^4S_{3/2}(\text{Si}^-) \rightarrow ^3P_0(\text{Si}) + e^-$ process, Ref. 5.

the experimental bond length of ground-state SiN⁻ could be in error by about a hundredth of an ångström.

The extrapolated binding energy of the $X^2\Sigma^+$ state of neutral SiN including core/valence effects, Douglas-Kroll-Hess scalar relativity, and atomic spin-orbit corrections is $D_e = 106.7$ kcal/mol, also in accordance with the experimental value of 109.6(3.2).⁴ A small discrepancy with the experiment is noted regarding the $A^2\Pi \leftarrow X^2\Sigma^+$ SiN energy splitting. Our calculations support that this energy separation amounts to about 1600 cm⁻¹, which is approximately 1.2 kcal/mol smaller than the experimentally observed value of 2032.4 cm⁻¹.³ Multireference configuration-interaction (MRCI) results from Cai *et al.*, with either cc-pVTZ or cc-pVQZ basis predict a better T_e gap (~ 2000 cm⁻¹),^{19,20} Table II, as compared with the experiment. Based on their calculated values for the T_1 diagnostic,²² Cai *et al.* have suggested that this difference with CCSD(T) is due to the quite different extent of nondynamical correlation in the two states.¹⁹ Their best $T_e = 2053$ cm⁻¹ comes from adding an estimated correction of this missing valence correlation to their extrapolated CCSD(T) results.

The experimental dissociation energy of the SiN $A^2\Pi$ state can be obtained by merely subtracting the $A^2\Pi \leftarrow X^2\Sigma^+$ (experimental) separation energy from the D_e value of the $X^2\Sigma^+$ state: $D_e(A^2\Pi) = 109.6(\pm 3.2)$ kcal/mol $- 2032.4$ cm⁻¹ = 103.8 \pm 3.2 kcal/mol, in harmony with our best value of $D_e = 102.1$ kcal/mol (Table II).

Table II also presents the calculated dipole moments for both $X^2\Sigma^+$ and $A^2\Pi$ states of SiN. Even though it was not possible to obtain extrapolated results, we believe that the values of 2.56($X^2\Sigma^+$) and 2.75 D($A^2\Pi$), very close to the RCCSD(T)/aug-cc-pwCV(5+d)Z results, are fairly accurate. Unfortunately, we were not able to find any experimental dipole moments for any of the two states of SiN.

Finally, CBS limit data are also presented in Table III for the bound excited $a^3\Sigma^+$ state of SiN⁻. Kalcher⁶ was the first to point out the existence of this bound state, lying 0.341 eV below the SiN $X^2\Sigma^+$ state at the MRACPF/cc-pVQZ level of theory. At the RCCSD(T)/aug-cc-pwCV(5+d)Z level, we find this energy difference equal to 0.242 eV. Our best results converge to the following D_e , $T_e(a^3\Sigma^+ \leftarrow X^1\Sigma^+)$, and r_e

TABLE II. Energies $E(E_h)$, binding energies D_e (kcal/mol), bond lengths r_e (Å), and dipole moments μ (D) for the $X^2\Sigma^+$ and $A^2\Pi$ states of SiN. Also shown are the adiabatic electron affinities EA(eV) of SiN and the $A^2\Pi \leftarrow X^2\Sigma^+$ excitation energy T_e (cm⁻¹). RCCSD(T) level of theory.

Basis set	E	D_e	r_e	μ	EA	E	D_e	r_e	μ	T_e	
			$X^2\Sigma^+$					$A^2\Pi$			
aug-cc-pVTZ	-343.607 646	98.88	1.5930	2.533	2.952	-343.601 243	94.86	1.6606	2.714	1405.2	
aug-cc-pVQZ	-343.627 962	103.75	1.5834	2.540	2.988	-343.621 049	99.41	1.6511	2.739	1517.1	
aug-cc-pV5Z	-343.634 959	105.65	1.5789	2.548	3.002	-343.627 937	101.24	1.6467	2.749	1541.2	
aug-cc-pV6Z	-343.637 194	106.23	1.5779	2.558	3.008	-343.630 169	101.83	1.6457	2.752	1541.8	
CBS(TQ56)		106.7(1)	1.5768(4)		3.011		102.2(1)	1.6446(4)			
CBS(TQ5)		106.6	1.5778		3.009		102.1	1.6456			
CBS(Q56)		106.8	1.5763		3.010		102.3	1.6441			
aug-cc-pVTZ-DKH	-344.239 856	98.70	1.5926		2.944	-344.233 472	94.69	1.6603		1401.1	
aug-cc-pVQZ-DKH	-344.260 453	103.57	1.5830		2.979	-344.253 556	99.24	1.6509		1513.7	
aug-cc-pV5Z-DKH	-344.267 539	105.46	1.5785		2.993	-344.260 531	101.06	1.6465		1538.1	
CBS(TQ5)		106.4	1.5774		2.999		101.9	1.6454			
aug-cc-pV(T+d)Z	-343.610 249	100.32	1.5868	2.527	2.947	-343.603 545	96.11	1.6546	2.733	1471.3	
aug-cc-pV(Q+d)Z	-343.629 296	104.46	1.5807	2.541	2.986	-343.622 273	100.06	1.6485	2.747	1541.3	
aug-cc-pV(5+d)Z	-343.635 256	105.78	1.5785	2.552	3.001	-343.628 210	101.36	1.6462	2.750	1546.3	
aug-cc-pV(6+d)Z	-343.637 335	106.30	1.5777	2.544	3.008	-343.630 301	101.88	1.6455	2.752	1543.8	
CBS(TQ56)		106.6	1.5772		3.011(1)		102.1	1.6450(1)			
CBS(TQ5)		106.9	1.5772		3.009		102.4	1.6450			
CBS(Q56)		106.5	1.5772		3.010		102.1	1.6449			
d-aug-cc-pV(T+d)Z	-343.610 775	100.60	1.5867	2.533	2.947	-343.604 057	96.39	1.6546	2.737	1474.4	
d-aug-cc-pV(Q+d)Z	-343.629 507	104.58	1.5806	2.542	2.986	-343.622 470	100.16	1.6485	2.748	1544.4	
d-aug-cc-pV(5+d)Z	-343.635 378	105.84	1.5785	2.553	3.001	-343.628 324	101.41	1.6462	2.751	1548.2	
d-aug-cc-pV(6+d)Z	-343.637 363	-106.31	1.5777	2.545	3.008	-343.630 326	101.90	1.6455	2.753	1544.4	
CBS(TQ56)		106.6	1.5773		3.011(1)		102.2	1.6450(1)			
CBS(TQ5)		106.9	1.5770		3.009		102.4	1.6450			
CBS(Q56)		106.6	1.5773		3.010		102.1	1.6449			
aug-cc-pwCV(T+d)Z	-343.875 634	101.46	1.5795	2.521	2.942	-343.868 509	96.99	1.6479	2.737	1563.8	
aug-cc-pwCV(Q+d)Z	-343.938 292	105.36	1.5745	2.534	2.985	-343.931 014	100.79	1.6427	2.747	1597.3	
aug-cc-pwCV(5+d)Z	-343.962 092	106.57	1.5730	2.554	3.000	-343.954 822	101.99	1.6411	2.748	1595.6	
CBS(TQ5)		107.6	1.5716		3.010		103.0	1.6397			
Δ_{CV}		+0.7	-0.0056		+0.001		+0.6	-0.0053			
Δ_{DKH}		-0.2	-0.0004		-0.010		-0.2	-0.0002			
Δ_{SO}		-0.4					-0.4				
Δ_{ZPE}^a					+0.001						
Best estimate		106.7	1.5713	2.56	3.002		102.1	1.6394	2.75	1600	
MP4SDQ ^b					3.326						
G2 ^c		105.6									
CISD ^d		74.3	1.556					1.625		-345	
CISD+Q ^e		88.6	1.568					1.640		663	
CCSD(T)/CBS+CV ^f			1.5724					1.6395		2053	
MRCI(0.01) ^g			1.5912	2.40				1.6569 ^h	2.53 ^h	1984 ^h	
MRCI(0.025) ⁱ		104.9 ^j	1.5809	2.58				1.6501	2.69	2099	
MRACPF ^k			1.5851		2.863						
Expt.		109.6(3.2) ^l	1.572 066(41) ^m		2.949(8) ⁿ		(103.8) ^o	1.641 879(20) ^p		2032.4(1) ^p 2008±65 ^q	

^aHarmonic zero-point energy correction.^bMøller-Plesset fourth-order perturbation theory with a (13s9p3d1f/5s11s7p2d1f/5s)→[10s7p3d1f/5s8s5p3d1f/5s] basis set, Ref. 7.^c D_0 value, Gaussian-2 theory, Ref. 18.^dSingles and doubles configuration interaction with Slater-type orbitals, Ref. 8.^eCISD+Davidson correction, Ref. 8.^fExtrapolated coupled cluster value+estimated core/valence contributions+approximate corrections for missing correlation energy, Ref. 19.^gMultireference configuration interaction (with a cutoff parameter of 0.01)/cc-pVTZ. Dipole moments obtained as expectation values, Ref. 19.^hContracted MRCI(0.01)/cc-pVTZ, Ref. 20.ⁱMRCI (with a cutoff parameter of 0.025)/cc-pVQZ, Ref. 20.^j D_e calculated as $D_0 + \omega_e/2$.^kMultireference-averaged coupled pair functional/cc-pVQZ, Ref. 6.^l $D_e = D_0 + \omega_e/2$, Ref. 4 (D_0) and Ref. 21 (ω_e).^mReference 2.ⁿReference 1.^oValue extracted indirectly as $D_e(A^2\Pi) = D_e(X^2\Sigma^+) - T_e$.^pReference 3.

TABLE III. Energies $E(E_h)$, binding energies D_e (kcal/mol), and bond lengths r_e (Å) for the $X^1\Sigma^+$ and $a^3\Sigma^+$ states of SiN^- , as well as the $a^3\Sigma^+ \leftarrow X^1\Sigma^+$ excitation energy T_e (cm^{-1}). RCCSD(T) level of theory.

Basis Set	E	D_e	r_e	E	D_e	r_e	T_e
		$X^1\Sigma^+$			$a^3\Sigma^+$		
aug-cc-pVTZ	-343.716 129	135.01	1.6112	-343.618 262	73.60	1.7371	21 479.3
aug-cc-pVQZ	-343.737 764	140.33	1.6022	-343.638 055	77.76	1.7249	21 883.6
aug-cc-pV5Z	-343.745 269	142.43	1.5979	-343.644 789	79.38	1.7193	22 052.8
aug-cc-pV6Z	-343.747 733	143.12	1.5970	-343.647 056	79.94	1.7179	22 096.0
CBS(TQ56)		143.6(1)	1.5959(4)		80.3	1.7166(4)	22 136.2(10.9)
CBS(TQ5)		143.4	1.5970		80.2	1.7178	22 118.9
CBS(Q56)		143.7	1.5954		80.3	1.7160	22 151.3
aug-cc-pVTZ-DKH	-344.348 030	134.81	1.6108	-344.250 187	73.41	1.7370	21 474.1
aug-cc-pVQZ-DKH	-344.369 945	140.13	1.6018	-344.270 259	77.57	1.7248	21 878.5
aug-cc-pV5Z-DKH	-344.377 537	142.22	1.5975	-344.277 080	79.19	1.7192	22 047.8
CBS(TQ5)		143.2	1.5966		80.0	1.7177	22 113.8
aug-cc-pV(T+d)Z	-343.718 554	136.36	1.6055	-343.620 149	74.61	1.7302	21 597.4
aug-cc-pV(Q+d)Z	-343.739 038	141.01	1.5997	-343.639 111	78.30	1.7218	21 931.4
aug-cc-pV(5+d)Z	-343.745 549	142.55	1.5975	-343.645 047	79.48	1.7188	22 057.6
aug-cc-pV(6+d)Z	-343.747 872	143.18	1.5967	-343.647 176	79.98	1.7176	22 100.2
CBS(TQ56)		143.5	1.5962		80.2	1.7170	22 128.0(2.2)
CBS(TQ5)		143.7	1.5963		80.4	1.7169	22 125.8
CBS(Q56)		143.4	1.5962		80.2	1.7170	22 131.1
d-aug-cc-pV(T+d)Z	-343.719 214	136.72	1.6054	-343.620 748	74.94	1.7300	21 610.8
d-aug-cc-pV(Q+d)Z	-343.739 317	141.16	1.5996	-343.639 346	78.43	1.7217	21 941.1
d-aug-cc-pV(5+d)Z	-343.745 720	142.64	1.5975	-343.645 197	79.56	1.7188	22 062.2
d-aug-cc-pV(6+d)Z	-343.747 915	143.20	1.5967	-343.647 224	80.01	1.7175	22 099.1
CBS(TQ56)		143.5	1.5963		80.2	1.7169(1)	22 126.6(4.3)
CBS(TQ5)		143.7	1.5962		80.5	1.7169	22 133.3
CBS(Q56)		143.5	1.5963		80.2	1.7171	22 132.7
aug-cc-pwCV(T+d)Z	-343.983 759	137.62	1.5984	-343.884 293	75.21	1.7231	21 830.3
aug-cc-pwCV(Q+d)Z	-344.047 990	142.11	1.5936	-343.947 116	78.81	1.7158	22 139.3
aug-cc-pwCV(5+d)Z	-344.072 356	143.53	1.5921	-343.970 985	79.92	1.7133	22 248.4
CBS(TQ5)		144.7	1.5908		80.9	1.7116	22 319.1
Δ_{CV}		+1.0	-0.0055		+0.5	-0.0053	193.3
Δ_{DKH}		-0.2	-0.0004		-0.2	-0.0001	-5.1
Best estimate		144.3	1.5904		80.5	1.7117	22 321
MP4SDQ ^a	-343.724 703	146.8	1.5940				
CISD ^b			1.573				
CISD+Q ^c			1.586				
MRACPF ^d			1.6045			1.7342	20 341 ^e
Expt.		145.5(3.4) ^e	1.604(5) ^f				

^aMøller-Plesset fourth-order perturbation theory with a $(13s9p3d1f/\text{Si}11s7p2d1f/\text{N}) \rightarrow [10s7p3d1f/\text{Si}8s5p3d1f/\text{N}]$ basis set, Ref. 7.

^bSingles and doubles configuration interaction with Slater-type orbitals, Ref. 8.

^cCISD+Davidson correction, Ref. 8.

^dMultireference-averaged coupled pair functional/cc-pVQZ, Ref. 6.

^eBinding energy calculated as $D_e(\text{SiN}^-) = D_0(\text{SiN}) + \text{EA}(\text{SiN}) - \text{EA}(\text{Si}) + \omega_e(\text{SiN}^-)/2$; Ref. 4 [$D_0(\text{SiN})$], Ref. 1 [$\text{EA}(\text{SiN})$, $\omega_e(\text{SiN}^-)$], and Ref. 5 [$\text{EA}(\text{Si})$].

^fReference 1.

^gCalculated as $\text{EA} - \Delta E[\text{SiN}(X^2\Sigma^+) - \text{SiN}^-(a^3\Sigma^+)]$.

values: 80.5 kcal/mol, 22 321 cm^{-1} , and 1.7117 Å. The corresponding Kalcher values are $T_e = 20 341 \text{ cm}^{-1}$ and $r_e = 1.7342 \text{ Å}$.⁶

IV. SUMMARY

Due to the first-ever availability of experimental results for SiN^- , the main purpose of the present work was to examine their validity by performing as accurate calculations as possible. Indeed, theory agrees very well with experiment with regard to the energetics (binding energies and electron affinity), but our theoretical results indicate that the experimental bond length of $\text{SiN}^-(X^1\Sigma^+)$ could have been overes-

timated by more than 0.01 Å. This is corroborated by the almost perfect agreement in the bond length between theory and experiment of the two lowest-lying states of the neutral SiN , $X^2\Sigma^+$ and $A^2\Pi$.

As a final remark, we wish to point out two things regarding extrapolations: (a) the “+d” basis sets offered slight improvement in the extrapolated values, as would have been expected. Indeed, the extrapolation is smoother with the added d function and the extrapolated values give quite negligible error bars. We note, however, that the actual CBS limit values do not differ that much between the two families (with and without the added d function) of basis sets. (b) The TQ56 and Q56 extrapolation schemes have much more in

common than the TQ5 extrapolation. The differences here are slight as well, the largest being 0.4 kcal/mol in binding energies and $\sim 0.001 \text{ \AA}$ in bond lengths. Of course, when Q56 extrapolation can be performed, it should be preferred over TQ5 and TQ56.

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