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Heat of formation of the SiF_2^{++} dication: a theoretical prediction

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Abstract

Energetics of the SiF_2^{++} dication and fragments related to it, SiF^{++} and SiF^{+}, was calculated using different ab initio approaches, including the semiempirically corrected G2, the complete basis set method, and the coupled cluster method up to the CCSD(T)/aug-cc-pVQZ level. The calculated values of bond energies and ionization potentials were carefully compared with the available experimental data to assess the accuracy of these approaches. In addition, reaction enthalpies for possible fragmentation reactions were calculated. The heat of formation of the SiF_2^{++} dication, resulting from these calculations, is $\Delta H_f(SiF_2^{++}) = 546 \pm 2$ kcal/mol and a theoretical estimate of $\Delta H_f(SiF^{++})$ is 649 ± 2 kcal/mol. (Int J Mass Spectrom 192 (1999) 165–171) © 1999 Elsevier Science B.V.

Keywords: Ab initio; Heat of formation; SiF^{++}; SiF_2^{++}; Dications

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1. Introduction

Long-lived polyatomic dications have attracted considerable attention from both experimentalists [1,2] and theoreticians [3,4]. Most of these dications are thermodynamically unstable doubly charged ions with respect to the corresponding pair of singly charged ions, and many of them rapidly dissociate. Only few long-lived (metastable with respect to dissociation into two singly charged products) polyatomic dications have been characterized experimentally so far. They sometimes exhibit unusual structures and reactivities and in this context they represent a challenging topic in gas phase ion chemistry. It has been shown that systems like CF_2^{++} and CF_3^{++} possess long-lived molecular states. Dications SiF_n^{++} represent a direct analogy to these systems and interesting insight may be obtained from a mutual comparison of their properties. Furthermore, a practical interest in the SiF_n^{+} and SiF_n^{++} series of cations and dications comes from their importance in plasma etching processes [5,6].

Neutral and singly charged systems SiF_n were studied over the last two decades by a variety of experimental and theoretical techniques [7–11]. Their energetics, spectroscopy, and reactivity are well known and well documented. However, the corresponding dications almost entirely escaped attention of theoreticians. O'Keeffe mentioned SiF_2^{++} in a

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theoretical study in 1986 [12]. However, all other studies of the dications appeared only very recently: SiF^{++} was studied by Kolbuszewski and Wright [13] using the multireference configuration interaction (MRCI) method and it was found to be thermodynamically stable; ab initio calculations of SiF^{++} formed a part of a study by Petrie [14], who investigated a series of dications using the G2 techniques. To our knowledge, no other theoretical studies on SiF_n^{++} have been reported.

Similarly, experimental studies of the SiF_n^{++} dications have been very rare. Heinemann [15] reported on the existence of a stable SiF^{++} in his mass spectrometric experiments and briefly mentioned an observation of a signal corresponding to SiF_2^{++}. In their pioneering studies, Price and co-workers [16] investigated photofragmentation reactions of SiF_2^{++} and SiF_3^{++} and dissociation processes of these ions in collisions with rare gases. According to their findings, the SiF_2^{++} and SiF_3^{++} dications suffer in the photodissociation process mainly a neutral particle loss yielding SiF^{++} and SiF_2^{++}, respectively. Similarly, doubly charged products dominate in collision reactions with He and Ne. Even in collisions with Ar, Kr, and Xe, where the charge transfer reaction to two singly charged products is exothermic, the neutral loss reactions can be observed. This was rationalized in terms of the symmetry distorted (C_{2v}) structure of SiF_3^{++} and the consequent unfavorable Franck-Condon factors for the formation of SiF_3^{+}. Participation of two electronic states of SiF_2^{++}, lying 31.0 ± 0.5 and 35.5 ± 0.5 eV above the energy of neutral SIF_2, in the fragmentation processes was suggested on the basis of application of a modified Landau-Zener model. In a subsequent paper [17], ab initio configuruation interaction single and double (CISD) and MRCI calculations of SiF_3^{++} were used to support the Landau-Zener modeling and to estimate vertical excitation energies of SiF_3^{++}.

In this article, we report on a theoretical treatment of the SiF_2^{++} dication using highly correlated and uniform levels of theory. We employed the coupled cluster method with a reasonably large and flexible basis set. This method is expected to provide relative energies with absolute errors of the order of only a few kcal/mol [18–20]. In order to crosscheck the results of our calculations, we followed the convergence of the results with the one-electron basis and critically compared the calculated data for the individual singly charged fragments with the energetics derived from experimental results. The main purpose of this study was to evaluate the thermochemistry of the SiF_2^{++} dication. This is important for evaluation and modeling of processes in semiconductor industry as well as for interpreting recent gas phase experiments. By combining the calculated and the experimental data we can provide a reliable value of the heat of formation of the SiF_2^{++} dication, $\Delta H_f(SiF_2^{++})$, and an estimation of $\Delta H_f(SiF^{++})$.

2. Computations

For the calculations the coupled cluster method {coupled cluster single double (triple) [CCSD(T)]} was used in conjunction with Dunning's correlation consistent basis sets (cc-pVTZ, aug-cc-pVTZ, cc-pVQZ, and aug-cc-pVQZ) as implemented in the GAUSSIAN94 [21] program. The geometry was preoptimized at the density functional level using the cc-pVTZ basis. The parametrized hybrid method due to Becke [22] involves a semiempirical combination of an "*exact*" (i.e. Hartree-Fock-like, but based on Kohn-Sham orbitals) exchange, the gradient-corrected Becke exchange [23], and the Lee-Yang-Parr correlation [24] functionals. The density functional theory (DFT) calculations were performed with the GAUSSIAN94 program. In analogy with the GAUSSIAN keywords, this approximate DFT method will be referred to as B3LYP. On the basis of our previous studies we expect that the geometries and energies calculated with the B3LYP method will be at least of the MP2/double zeta polarization (MP2/DZP) quality [25–27] and should serve as good initial estimates for the CCSD(T) calculations.

The CCSD(T) calculations were performed with the Gaussian program in the corresponding "restricted" CCSD(T) and "unrestricted" CCSD(T) modes. All valence electrons were correlated in these calculations. The geometry was optimized using numerical first and second derivatives of energy, starting from the structures obtained by the B3LYP method. Vibrational frequencies were calculated using numerical second derivatives at the CCSD(T)/cc-pVTZ level. In addition, the approximate G2 method (as introduced by Pople and co-workers [28]) and the complete basis set method (CBS) of Petersson [29] was used for completeness and to account for the origin of different residual basis set errors.

3. Results and discussion

The geometries obtained by the particular methods are listed in Tables 1 and 2. For the approximate methods CBS and G2 the geometries listed in Tables 1 and 2 correspond to those calculated at the HF level of theory. The MP2 value, on which the G2 energy calculation was carried out, is listed separately. The HF values are not far both from the results obtained by the correlated methods and from experimental values. Consequently, the corresponding G2 and CBS energies should be reliable. However, this statement is not general: it has been reported recently [14] that for dications the G2 (and consequently the CBS) approach may lead to unreliable results. The unscaled HF calculated harmonic frequencies are slightly overestimated and they are listed only for completeness. An inspection of the data in the Tables 1 and 2 shows that the results of the correlated methods are in good agreement with each other. The B3LYP values agree rather well with the MP2 results. The bond lengths progressively decrease, as the basis set is improved and more advanced methods are used. Furthermore, the geometries for SiF and SiF_2, calculated at the CCSD(T) level, converge to the experimental values [30] with the extension of the basis set. The CCSD(T)/aug-cc-pVQZ calculations give for the bond length of SiF ($^2\Pi$ state; spin density Si 0.98) the value of 1.613 Å, in good agreement with the experimental value of 1.601 Å. This agreement becomes almost quantitative when the augmented quintuple zeta quality basis set (aug-cc-pV5Z) is used in the CCSD(T) calculation (1.608 Å [7]).

For SiF_2 ($X\ ^1A_1$) the CCSD(T)/aug-cc-pVQZ calculation results in a Si–F bond length of 1.602 Å and in a F–Si–F angle of 100.5°. The corresponding experimental data are 1.591 Å and 100.98°, respectively [30]. Unfortunately, we could not afford to optimize the geometry at the CCSD(T)/aug-cc-pV5Z level and due to prohibitively high computational costs the calculation of the harmonic frequencies was done only with the small basis set. However, the CCSD(T)/cc-pVTZ and B3LYP/cc-pVTZ calculations gave frequency values differing only by a few wave numbers from the experimental results.

The geometry of the corresponding triplet state ($a\ ^3B_1$) is not known experimentally. However, Karolczak et al. [31] have reported recently the value of 278.2 cm^{-1} for the symmetric bending frequency (a_1) of this state in the gaseous phase. This number is well reproduced in our CCSD(T)/cc-pVTZ calculations. In addition, the corresponding adiabatic singlet–triplet transition, known from experiments to be 3.25 eV, was calculated as 3.19 eV at the CCSD(T)/cc-pVTZ and as 3.31 eV at the G2 level.

The Si–F bond is slightly shortened upon ionization. In SiF^+ ($^1\Sigma$) its value is 1.537 Å at the CCSD(T)/cc-pVQZ level. Similarly to the neutral case, this value is only marginally shortened when the basis set is extended to aug-cc-pV5Z (1.533 Å [7]). Recently, Woods and co-workers [32] have reported for the SiF^+ cation the vibrational frequency of 1050.4 cm^{-1} associated with the bond length of 1.527 Å. Our calculated values are thus again higher by about 0.01 Å. Fortunately, the effect on the relative energies is small and we probably profit here from an error cancellation. The calculated ionization energy (IE) at the highest level employed [CCSD(T)/aug-cc-pVQZ] is 7.35 eV, in agreement with the G2 value of 7.34 eV. The two reported experimental values are 7.54 ± 0.16 eV (obtained by Weber and Armentrout [33]) and 7.28 eV (reported by Huber and Herzberg [34]) bracket these calculated values quite well. A further indication of the quality of our calculated results is the $^1\Sigma \rightarrow {}^3\Pi$ separation for SiF^+: it is 4.69 eV on the [CCSD(T)/aug-cc-pVTZ] level, in agreement with the previously reported MRCI value of 4.77 eV [13].

For SiF_2^+ ($X\ ^2A_1$) our calculations give the SiF

Table 1
Calculated data for SiF, SiF^+, and SiF^{++}

	Total energy [Hartree]	R (Å)	Frequency (cm^{-1})
SiF ($^2\Pi$)			
CBS	−388.807 795	1.598	995.7 (σ_g)
G2	−388.787 005	1.605	918.5 (σ_g)
MP2/6-31G*	−388.585 225	1.627	
B3LYP/cc-pVTZ	−389.380 854	1.628	830.2 (σ_g)
CCSD(T)/cc-pVTZ	−388.766 356	1.619	854.1 (σ_g)
CCSD(T)/aug-cc-pVTZ	−388.778 836	1.624	
CCSD(T)/cc-pVQZ	−388.809 475	1.611	
CCSD(T)/aug-cc-pVQZ	−388.813 996	1.613	
exp		1.601[a]	
SiF ($^4\Sigma$)			
CBS	−388.679 379	1.613	963.9 (σ_g)
G2	−388.652 563	1.611	921.9 (σ_g)
B3LYP/cc-pVTZ	−389.239 982	1.637	813.6 (σ_g)
CCSD(T)/cc-pVTZ	−388.636 159	1.626	851.5 (σ_g)
SiF^+ ($^1\Sigma$)			
CBS	−388.540 094	1.538	1169.3 (σ_g)
G2	−388.517 114	1.533	1104.5 (σ_g)
MP2/6-31G*	−388.333 729	1.559	
B3LYP/cc-pVTZ	−389.106 937	1.552	1005.1 (σ_g)
CCSD(T)/cc-pVTZ	−388.499 251	1.546	1034.4 (σ_g)
CCSD(T)/aug-cc-pVTZ	−388.508 641	1.547	
CCSD(T)/cc-pVQZ	−388.540 188	1.537	
CCSD(T)/aug-cc-pVQZ	−388.543 753	1.538	
exp			1050 (σ_g)[b]
SiF ($^3\Pi$)			
CBS	−388.366 686	1.557	1093.4 (σ_g)
G2	−388.340 397	1.548	1061.2 (σ_g)
B3LYP/cc-pVTZ	−388.877 284	1.628	862.9 (σ_g)
CCSD(T)/cc-pVTZ	−388.636 159	1.564	
SiF^{++} ($^2\Sigma$)			
CBS	−387.768 667	1.516	1155.8 (σ_g)
G2	−387.742 529	1.484	1152.6 (σ_g)
MP2/6-31G*	−387.577 183	1.532	
B3LYP/cc-pVTZ	−388.334 014	1.529	997.5 (σ_g)
CCSD(T)/cc-pVTZ	−387.729 871	1.519	1060.9 (σ_g)
CCSD(T)/aug-cc-pVTZ	−387.738 494	1.519	
CCSD(T)/cc-pVQZ	−387.769 561	1.508	
CCSD(T)/aug-cc-pVQZ	−387.772 961	1.509	

	IP(SiF) [eV]	IP(SiF^+) [eV]	IE2 (SiF_2) [eV]	ΔH_f (kcal/mol)
CBS	7.28	20.99	28.28	647
G2	7.34	21.08	28.42	651
MP2/6-31G*	6.84	20.59	27.43	628
B3LYP/cc-pVTZ	7.45	21.03	28.49	652
CCSD(T)/cc-pVTZ	7.27	20.94	28.20	646
CCSD(T)/aug-cc-pVTZ	7.35	20.96	28.31	648
CCSD(T)/cc-pVQZ	7.33	20.97	28.30	648
CCSD(T)/aug-cc-pVQZ	7.35	20.97	28.33	648
exp	7.28[c]–7.54[d]			

[a] [30].

[b] [32].

[c] [34].

[d] [33].

Table 2
Calculated data for SiF$_2$, SiF$_2^+$, and SiF$_2^{++}$

	Total energy [Hartree]	R (Å)	α	Frequencies (cm^{-1})		
SiF$_2$ (^{1}A$_1$)						
CBS	−488.704 01	1.587	99.2	393.1 (a$_1$)	1006.1 (a$_1$)	1035.7 (b$_2$)
G2	−488.664 56	1.592	99.6	372.6 (a$_1$)	933.0 (a$_1$)	950.6 (b$_2$)
MP2/6F-31G*	−488.321 05	1.616	100.9			
B3LYP/cc-pVTZ	−489.382 55	1.617	100.5	330.4 (a$_1$)	836.0 (a$_1$)	845.3 (b$_2$)
CCSD(T)/cc-pVTZ	−488.625 37	1.608	100.8	351.5 (a$_1$)	849.5 (a$_1$)	866.2 (b$_2$)
CCSD(T)/aug-cc-pVTZ	−488.647 75	1.612	100.2			
CCSD(T)/cc-pVQZ	−488.705 74	1.602	100.5			
CCSD(T)/aug-cc-pVQZ	−488.714 01	1.602	100.5			
exp		1.591[a]	100.9[a]	345 (a$_1$)[a]	855 (a$_1$)[a]	870 (b$_2$)[a]
SiF$_2$ (^{3}B$_1$)						
CBS	−488.589 11	1.593	112.9	302.3 (a$_1$)	945.1 (a$_1$)	1082.9 (b$_2$)
G2	−488.543 01	1.593	113.9	295.4 (a$_1$)	893.2 (a$_1$)	102.2 (b$_2$)
MP2/6-31G*	−488.206 09	1.617	115.8			
B3LYP/cc-pVTZ	−489.265 17	1.615	114.1	260.5 (a$_1$)	799.8 (a$_1$)	916.4 (b$_2$)
CCSD(T)/cc-pVTZ	−488.508 19	1.606	113.2	272.4 (a$_1$)	834.0 (a$_1$)	948.7 (b$_2$)
exp				278.2 (a$_1$)[b]		
SiF$_2^+$ (^{2}A$_1$)						
CBS	−488.306 71	1.536	116.8	329.8 (a$_1$)	1059.2 (a$_1$)	1260.0 (b$_2$)
G2	−488.264 31	1.527	118.2	334.4 (a$_1$)	1017.2 (a$_1$)	1211.2 (b$_2$)
MP2/6-31G*	−487.946 75	1.555	119.9			
B3LYP/cc-pVTZ	−488.987 81	1.549	119.8	283.6 (a$_1$)	906.4 (a$_1$)	1091.8 (b$_2$)
CCSD(T)/cc-pVTZ	−488.234 19	1.542	120.1			
CCSD(T)/aug-cc-pVTZ	−488.252 38	1.544	119.9			
CCSD(T)/cc-pVQZ	−488.312 25	1.536	119.9			
CCSD(T)/aug-cc-pVQZ	−488.318 87	1.536	119.9			
SiF$_2^{++}$ ($^1\Sigma_g$)						
CBS	−487.606 62	1.503	180	210.4 (π_g)	948.1 (σ_g)	1481.1 (σ_u)
G2	−487.567 81	1.484	180	242.1 (π_g)	950.6 (σ_g)	1476.8 (σ_u)
MP2/6-31G*	−487.256 38	1.520	180			
B3LYP/cc-pVTZ	−488.282 58	1.506	180	227.9 (π_g)	868.1 (σ_g)	1339.8 (σ_u)
CCSD(T)/cc-pVTZ	−487.541 54	1.503	180			
CCSD(T)/aug-cc-pVTZ	−487.557 74	1.505	180			
CCSD(T)/cc-pVQZ	−487.615 71	1.496	180			
CCSD(T)/aug-cc-pVQZ	−487.622 48	1.496	180			

	IP(SiF$_2$) [eV]	IP(SiF$_2^+$) [eV]	S → T [eV]	IE2 (SiF$_2$) [eV]	ΔH_f (kcal/mol)
CBS	10.81	19.05	3.13	29.86	548
G2	10.89	18.95	3.31	29.84	548
MP2/6-31G*	10.19	18.79	3.13	28.97	528
B3LYP/cc-pVTZ	10.74	19.19	3.19	29.93	550
CCSD(T)/cc-pVTZ	10.64	18.85	3.19	29.49	540
CCSD(T)/aug-cc-pVTZ	10.76	18.90		29.66	543
CCSD(T)/cc-pVQZ	10.71	18.95		29.66	544
CCSD(T)/aug-cc-pVQZ	10.75	18.95		29.70	544
exp	10.78[c]		3.25[d]		

[a] [30].
[b] [31].
[c] [35].
[d] [30].

bond length of 1.536 Å at the CCSD(T)/aug-cc-pVQZ level. Since the CCSD(T)/aug-cc-pV5Z calculations require a prohibitively high CPU time costs and the gain in accuracy was expected to be only marginal, we kept the computation on the CCSD(T)/aug-cc-pVQZ level. The ionization energy calculated at this level, 10.74 eV, is almost identical with the photoionization value of 10.78 ± 0.05 eV [35].

In general, it appears that the directly calculated ionization energies are reliable within an error of less than ±0.1 eV. As noted earlier in our work on CF_2^{++} [36], the largest deviation in calculated IE was found for the fluorine atom, where the role of the one-electron basis was found essential. However, the CCSD(T)/aug-cc-pVQZ calculations give IE (F) of 17.34 eV, close to the recent experimental value of 17.42 eV. Thus even here the results are within the required error bars. A further confirmation of the accuracy of the chosen theoretical approach is the calculation of the Si-F bond energy in neutral SiF_2. The value of D_0(FSi–F) calculated by the CCSD(T)/aug-cc-pVQZ method is 154.4 kcal/mol (D_e = 152.7 kcal/mol). With the use of very recent tabulated values of heats of formation [37] [$\Delta H_f(SiF_2) = -140.5$ kcal/mol, ΔH_f(SiF) = −4.8 kcal/mol, and ΔH_f(F) = 19.0 kcal/mol) we obtain D_0(FSi–F) = 154.7 kcal/mol. These results are very encouraging in assessing the reliability of the CCSD(T) method.

Finally, it should be noted that the results obtained by the B3LYP method follow the ab initio trends. The absolute errors are smaller than for MP2, being about ±0.3 eV. It is known, however, that—in contrast with the methods based on the wave function—the effect of the incomplete basis is much smaller for the DFT approaches [38–41]. Therefore, unlike in the MP2 approach, we do not expect any further improvement of the DFT results when using larger than cc-pVTZ basis sets. Thus this DFT approach seems to be less suitable for energy calculations of dications. On the other hand, those few examples that we have for the values of frequencies calculated by the B3LYP method (also for CF_2^{++} [36] and CF_3^{++} [42]), and which come out only slightly smaller than the corresponding CCSD(T) values, confirm that this method can describe well both the structural properties and the shape of the surface in the minimum region.

Calculations concerning the two dications SiF^{++} and SiF_2^{++} are summarized in Tables 1 and 2, too. Upon double ionization, the Si–F bond is shortened to 1.509 Å for SiF^{++} (spin densities Si 0.86 and F 0.14), and to 1.496 Å for SiF_2^{++}. The former value is in a rather good agreement with the recent MRCI calculation of Kolbuszewski and Wright (1.507 Å) [13]. No information is available on the structure of SiF_2^{++}. However, by extrapolating the results for the neutral and the singly charged species, one may expect that the Si–F bonds are somewhat shorter than the calculated values.

The values of IE(SiF^+) converge with the increasing basis sets towards 20.97 eV, while the calculated value of IE(SiF_2^+) appears to be slightly smaller, 18.98 eV. The calculated value of the double-ionization energy IE($SiF_2 \rightarrow SiF_2^{++}$) is then 29.70 eV. This is in good agreement with experimental values: In 1980 Tsai and Eland obtained 1980 by a direct measurement 31.4 eV [43], and recently Lee et al. [16] have estimated—on the basis of the Landau-Zener theory—the value of 31.0 ± 0.5 eV. The stability of SiF_2^{++} appears to be quite remarkable: for the dissociation to $SiF^+ + F^+$ we obtain the dissociation energy (D_e) of 39.6 kcal/mol at the CCSD(T)/aug-cc-pVQZ level (35.6 kcal/mol at G2). The dissociation to SiF^{++} + F requires an energy of 123.3 kcal/mol. Moreover, assuming the existence of a barrier resulting from the avoided crossing with the coulombic potential energy surface correlating with the asymptote $SiF^+ + F^+$, the dication SiF_2^{++} should exhibit a considerably long lifetime.

The abovementioned good results in calculating the ionization energies make it possible to give an estimate of the heat of formation of both dications. It is difficult to assign rigorous error bars; however, a conservative estimate of the errors of our calculations is ±0.1 eV (±2 kcal/mol). Ricca and Bauschlicher [7] came to similar conclusions on the basis of the CCSD(T) calculated atomization energy of SiF_4. Combining the heat of formation of SiF_2 (−140.5 ± 2 kcal/mol [37]) and the calculated IE value leads to ΔH_f (SiF_2^{++}) of 546 ± 2 kcal/mol. The heat of formation of SiF^{++} could be estimated in principle in the same way. Unfortunately, recent experimental values of ΔH_f(SiF) vary from $+1.7$ kcal/mol to -14.2 kcal/mol [7] and thus the uncertainty in the estimation of ΔH_f (SiF^{++}) is much higher. With the use of the most recent value, ΔH_f (SiF) $= -4.8$ kcal/mol [37], we can estimate ΔH_f (SiF^{++}) $= 649 \pm 2$ kcal/mol.

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