Experimental and Theoretical Studies on SiH_n^{2+} Dications (n = 1—5)[1]

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Ab initio molecular orbital calculations, executed at the MP4/6-31G**//6-31G* level, were performed for SiH_n^{2+} dications (n = 1—5). In line with charge-stripping mass spectroscopic experiments both SiH^{2+} and SiH_2^{2+} are stable ions. Depending on the chemical precursor [*i.e.* $Si(CH_3)_4$ or SiH_4] either the singlet ground state or the lowest triplet state of SiH^+ are involved in the charge-stripping process. Moreover, electron impact ionization of SiH_4 directly generates two stable states of SiH^{2+}. For the system SiH_2^+–SiH_2^{2+}, however, there is no experimental evidence for the involvement of excited states in the charge-stripping process. SiH_3^{2+} is also an experimentally accessible dication; however, the experimentally derived Q_{min} value and the theoretically predicted vertical ionization energy differ significantly for SiH_3^{2+}, while they are in good to excellent agreement for SiH^{2+} and SiH_2^{2+}, respectively. Owing to the lack of suitable cationic precursors no experimental data are available for SiH_4^{2+} and SiH_5^{2+}. The calculations predict these species to be weakly bound complexes of SiH_2^{2+} and atomic and molecular hydrogen respectively.

The gas-phase chemistry of multiply charged ions has become an interesting and challenging field for both experimentalists and quantum chemists. In particular, doubly charged dications have attracted much attention in the last few years. By means of charge-stripping (c.s.) mass spectrometry[2] it became possible to generate a large number of dications, having lifetimes of several microseconds. Among these unusual ions are very small ones, whose coulombic repulsion is expected to be quite substantial.[2] However, these experimental techniques are able only to prove the existence of a particular dication and to determine the minimum energy required to generate it from the corresponding monocation. Accordingly, they are not suited for detailed characterization of the structural and other features of this remarkable class of molecules. On the other hand high level *ab initio* calculations have turned out to be an extremely useful tool for elucidating the gas-phase chemistry of dications.[3] Using this combined experimental–theoretical approach we have already studied several dications, and the agreement between experimentally derived data and theoretical predictions are in most cases excellent.[4] In this paper we report our results on SiH_n^{2+} species (n = 1—5), which were in part already studied experimentally by Beynon *et al.*[5]

Experimental

Charge-stripping experiments have been used to determine the Q_{min} value for generating SiH_n^{2+} from the corresponding SiH_n^+ monocations. The latter were generated from SiH_4 or $Si(CH_3)_4$ *via* electron impact ionization (20 and 70 eV, see below) using a VG analytical ZAB-2F mass spectrometer in which the magnetic sector precedes the electrostatic sector. Mass-separated SiH_n^+ ions of 8 KeV energy were made to collide with O_2 at a pressure of *ca.* 10^{-4} Torr. The products of the collision-induced reactions were studied by scanning the electrostatic analyser. For an accurate measurement of Q_{min}, the energy scale was calibrated by admitting toluene as a reference compound for which $Q_{min.}$ is known to be 15.7 eV for the process $C_7H_8^+ \longrightarrow C_7H_8^{2+}$.[6] The $Q_{min.}$ value was obtained by extrapolating to the base line of the high energy of both the main beam (SiH_n^+ ions) and the charge-stripping peak as recommended by Beynon and his co-workers.[2b] The elemental composition of the SiH_n^+ ions have been determined by Fourier transform ion cyclotron resonance (f.t.–i.c.r.) technique using a Bruker CMS 47 instrument which was tuned for this experiment to a mass resolution of $M/\Delta M$ = 330,000.

Calculations

Standard *ab initio* molecular orbital calculations were carried out using the CRAY version of the GAUSSIAN 82 series of programs.[7] Optimized geometries and harmonic vibrational frequencies were obtained with the *d*-polarized 6-31G* basis set[8] whereas single-point calculations on the optimized geometries were performed with the *d,p*-polarized 6-31G** basis set.[8] Effects of valence electron correlation were incorporated by means of Møller–Plesset perturbation theory up to full fourth order.[9] This level of theory will be referred to as MP4/6-31G**//6-31G*. In order to check the applicability of these standard basis sets we reoptimized the scale factors of 6-31G* for SiH_2^{2+}. The so-obtained optimal 6-31G* basis for SiH_2^{2+} led to a decrease in total energy of only 1.69 mHartree (*i.e.* 1.1 kcal mol^{-1}) with respect to the standard 6-31G* value. Because this improvement is chemically irrelevant we decided, for the sake of consistency, to use the standard basis set throughout.

Results and Discussion

Optimized structures (bond lengths in Angstrøms, bond angles in degrees) are displayed in Figure 1 and energies [total energies in Hartrees, zero-point vibrational energies (ZPVE)[10] in kcal mol^{-1}] obtained at the various levels of theory are summarized in Table 1. Energies in the text refer to MP4/6-31G**//6-31G* and structural parameters to the 6-31G* values. In distinct contrast to the valence isoelectronic CH^{2+} dication, which has a purely repulsive ground-state potential[11] or, at most, a very shallow energy dip,[12] the $^2\Sigma^+$ ground state of SiH^{2+} (**1**) was found to be clearly a minimum. While the bond length for SiH^{2+} was calculated to be longer (1.642 Å) compared with the monocationic (1.486 Å) and neutral (1.515 Å) SiH species, the calculated harmonic frequency of 1 121 cm^{-1} is rather high.

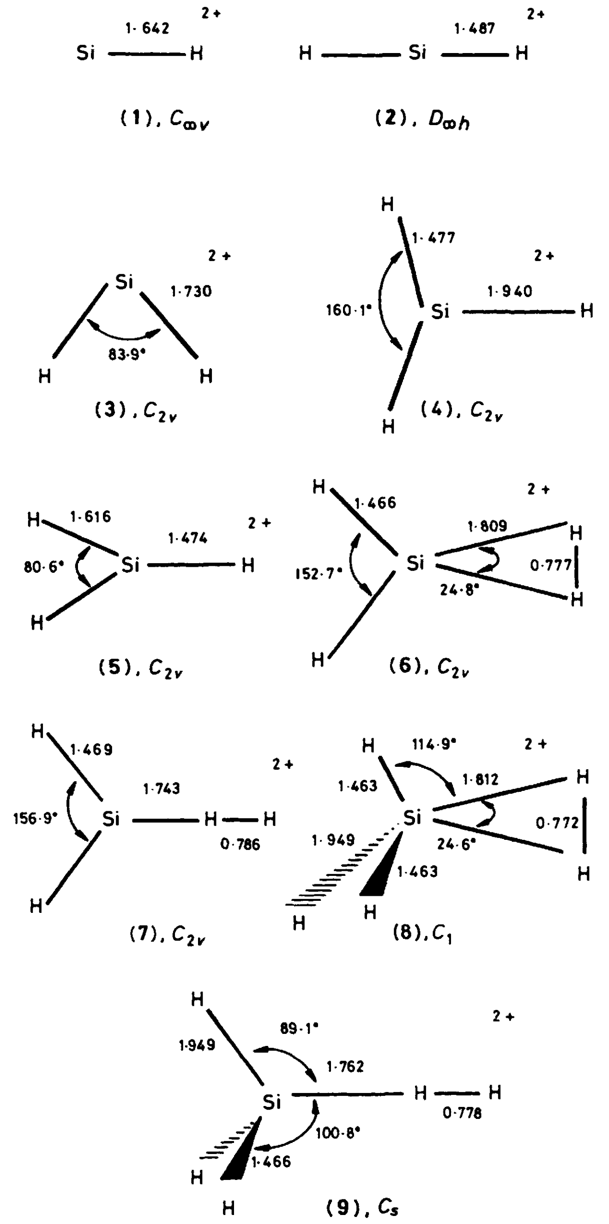

Figure 1. 6-31G* optimized geometries of the SiH_n^{2+} dications

Moreover a substantial barrier of 1.07 eV for the charge-separation reaction is predicted in a detailed multi-reference configuration interaction (c.i.) investigation of this species, which will be published separately.[13] The theoretically predicted stability of SiH^{2+} is in perfect agreement with the findings of Beynon *et al.*[5] and our own experiments in which SiH^{2+} is found as a stable dication. By using $Si(CH_3)_4$ as a precursor for generating cationic SiH^+ we obtain a $Q_{min.}$ value of 18.8 eV, almost identical to the $Q_{min.}$ value of 18.7 eV reported by Beynon *et al.*,[5] who employed the same experimental conditions. Using SiH_4 as the neutral precursor to generate SiH^+, the same $Q_{min.}$ value is only found when a rather low ionization energy of 20 eV is employed. At higher ionization energy (70 eV) a new state of SiH^+ becomes populated, thus resulting in a lower $Q_{min.}$ value of 16.5 eV, as clearly depicted in Figure 2.

This interesting observation is completely in line with our calculations. To model the c.s. experiments theoretically, we computed the vertical ionization energy of SiH^+ which then can be compared with the $Q_{min.}$ value. If the vertical transition involves the $^1\Sigma^+$ ground state of SiH^+ an ionization energy of 18.3 eV results, whereas for the transition from the first excited state of SiH^+, which is the lowest triplet state ($^3\Pi$), a vertical ionization energy of 16.1 eV is predicted. Thus, SiH^+ provides another striking example that the c.s. process does not necessarily involve only the ground state of a particular cation, but that excited states may also be of importance.* It should be mentioned that not only SiH^+ but also the dication, *i.e.* SiH^{2+}, exists in two stable electronic states, $X^2\Sigma^+$ and $A^2\Pi$ in line with theoretical predictions.[13] Experimental evidence for this is provided by the analysis of the MIKE spectrum[14] of SiH^{2+} generated in the ion source upon 70 eV electron impact ionization of SiH_4. The signal corresponding to the reaction $SiH^{2+} \longrightarrow Si^+ + H^+$ is of composite nature [two distinct peaks centred at (28/29) × $2E_0$]; this observation is, indeed, best accounted for by assuming that two states of SiH^{2+} are involved in the dissociation process. From the kinetic energy release, *T*, associated with this reaction one can derive to a first approximation the intercharge distance, *r*, of the two singly charged species, *i.e.* Si^+ and H^+, at the time of separation by using the simple equation $T(\text{eV}) = 14.4/r(\text{Å})$.[14b] The *T* values measured at the horns of the dished peaks are for the narrow component, $T_h = 2.42$ eV, and $T_h = 8.39$ eV for the broad one, which in turn give $Si^+ \cdots H^+$ distances of 5.98 and 1.74 Å, respectively. The multi-reference (c.i.) study of SiH^{2+} predicts[13] for the transition state of the $X^2\Sigma^+SiH^{2+}$ species, dissociating to Si^+ and H^+, a value of $r > 5.5$ Å, while that predicted for the excited $A^2\Pi SiH^{2+}$ species is *ca.* 2 Å. Moreover, if one assumes that T_h, to a first approximation, equals the reverse activation energy,[15] *i.e.* the combination of Si^+ and H^+, the fit between experimental data and predicted numbers is excellent. The c.i. study[13] for the process $Si^+ + H^+ \longrightarrow SiH^{2+}(X^2\Sigma^+)$ gives an activation energy of 2.5 eV, which should be compared with $T_h = 2.42$ eV.

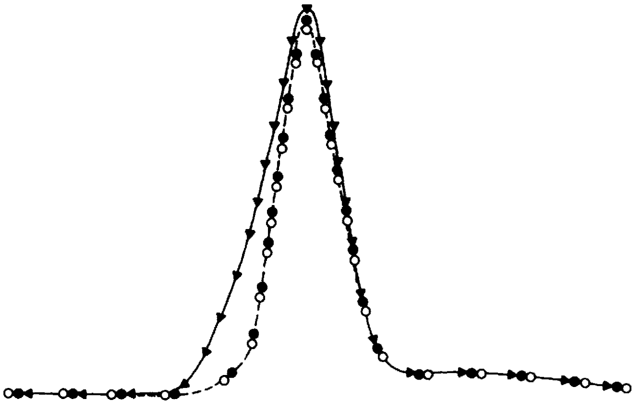

Figure 2. Charge-stripping spectrum representing the process $SiH^+ + O_2 \longrightarrow SiH^{2+} + O_2 + e^-$ [▼ precursor SiH_4, 70 eV; ● precursor $Si(CH_3)_4$, 70 eV; ○ precursor SiH_4, 20 eV]

For SiH_2^{2+} our calculations predict two distinct minima, a linear singlet structure (**2**) and a C_{2v} triplet species (**3**), the former being 62.4 kcal mol^{-1} more stable than the latter. The singlet has a remarkable short Si–H bond of only 1.487 Å, even shorter than in neutral SiH_2 (1.510 Å). SiH_2^{2+}, too, should be prevented from spontaneous deprotonation. The short bond and the relatively high frequency of the antisymmetric Si–H

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* For a similar case see ref. 4*i*.

Table 1. Total energies (Hartrees) and zero-point vibrational energies (ZPVE, kcal mol^{-1})

Molecule	Symmetry	6-31G*^{a}	6-31G**^{a}	MP2/6-31G**^{a}	MP3/6-31G**^{a}	MP4/6-31G**^{a}	ZPVE^{a,b}
SiH^{2+} (**1**)	$C_{\infty v}$	−288.498 77	−288.501 59	−288.531 98	−288.541 08	−288.544 70	1.6
SiH^{+} (singlet)	$C_{\infty v}$	−289.136 46	−289.138 17	−289.194 00	−289.209 07	−289.214 23	
SiH^{2+} (vert)	$C_{\infty v}$		−288.497 75	−288.528 29	−288.536 90	−288.540 12	
SiH^{+} (triplet)	$C_{\infty v}$	−289.079 20	−289.081 12	−289.119 14	−289.129 21	−289.132 72	
SiH^{2+} (vert)	$C_{\infty v}$		−288.498 10	−288.528 64	−288.537 27	−288.540 51	
SiH_2^{2+} (singlet) (**2**)	$C_{\infty v}$	−289.109 58	−289.114 19	−289.167 13	−289.179 03	−289.182 58	7.7
SiH_2^{2+} (triplet) (**3**)	C_{2v}	−289.020 64	−289.026 79	−289.061 77	−289.071 89	−289.075 95	3.2
SiH_2^{+}	C_{2v}	−289.709 83	−289.713 33	−289.771 98	−289.785 25	−289.789 23	
SiH_2^{2+} (singlet, vert)	C_{2v}		−289.071 79	−289.127 58	−289.140 52	−289.144 66	
SiH_3^{2+} (**4**)	C_{2v}	−289.632 04	−289.639 92	−289.696 30	−289.708 85	−289.712 63	9.6
SiH_3^{2+} (**5**)	C_{2v}	−289.623 62	−289.631 29	−289.689 69	−289.703 30	−289.707 95	8.6
SiH_3^{+} (singlet)	D_{3h}	−290.328 91	−290.333 99	−290.413 69	−290.430 23	−290.434 67	
SiH_3^{2+} (vert)	D_{3h}		−289.589 83	−289.648 15	−289.662 22	−289.667 23	
SiH_3^{+} (triplet)	C_s	−290.212 76	−290.217 34	−290.278 41	−290.291 99	−290.296 11	
SiH_3^{2+} (vert)	C_s		−289.592 30	−289.651 00	−289.664 37	−289.668 69	
SiH_4^{2+} (**6**)	C_{2v}	−290.270 86	−290.286 27	−290.370 63	−290.388 20	−290.393 01	17.5
SiH_4^{2+} (**7**)	C_{2v}	−290.269 00	−290.275 78	−290.360 85	−290.378 88	−290.384 12	16.8
SiH_5^{2+} (**8**)	C_1	−290.789 76	−290.807 86	−290.896 21	−290.914 41	−290.919 50	19.6
SiH_5^{2+} (**9**)	C_s	−290.787 33	−290.797 19	−290.885 80	−290.904 35	−290.909 82	19.0

[a] At 6-31G* optimized geometries. [b] Scaled by 0.9, see ref. 10.

Table 2. Isotopic distribution at *m*/*z* 29, 30, and 31 in the 70 eV mass spectrum of SiH_4

Precursor	*m*/*z* 29	*m*/*z* 30	*m*/*z* 31
SiH_4	$^{29}Si^{+} = 5.7\%$	$^{30}Si^{+} = 1.2\%$	$^{30}SiH^{+} = 1.3\%$
	$^{28}SiH^{+} = 94.3\%$	$^{29}SiH^{+} = 1.6\%$	$^{29}SiH_2^{+} = 6.6\%$
		$^{28}SiH_2^{+} = 97.2\%$	$^{28}SiH_3^{+} = 92.1\%$
$Si(CH_3)_4$	$^{29}Si^{+} = 3.0\%$	$^{30}Si^{+} = 16.7\%$	$^{30}SiH^{+} = 5.3\%$
	$^{28}SiH^{+} = 97.0\%$	$^{29}SiH^{+} = 52.8\%$	$^{29}SiH_2^{+} = 0.0\%$
		$^{28}SiH_2^{+} = 30.5\%$	$^{28}SiH_3^{+} = 94.7\%$

stretching mode (2 021 cm^{-1}) indicate an even higher barrier than for SiH^{2+}. In fact, SiH_2^{2+} is easily accessible by charge stripping from SiH_2^{+}. However, the $Q_{min.}$ value reported by Beynon *et al.*[5] using $Si(CH_3)_4$ as the neutral precursor to generate SiH_2^{+} and our result by using SiH_4 as the precursor differ significantly, being 17.7 and 16.7 eV, respectively. To elucidate this surprising difference we performed a high-resolution experiment using f.t.—i.c.r. on the corresponding SiH_n^{+} ions from both neutral precursors. The results, given in Table 2, reveal the following. Whereas *m*/*z* = 29 consists of over 90% of the desired species, *i.e.* $^{28}SiH^{+}$, irrespective of the precursor used, for *m*/*z* = 30 only SiH_4 represents a useful precursor generating 'pure' $^{28}SiH_2^{+}$. $Si(CH_3)_4$ yields just 30.5% of the desired cation and the majority of the peak consists of $^{29}SiH^{+}$. Thus, the $Q_{min.}$ value for SiH_2^{+} of Beynon *et al.*[5] derived from $Si(CH_3)_4$ as the neutral precursor does not correspond to $^{28}SiH_2^{+}$ but to a mixture of $^{28}SiH_2^{+}$ and $^{29}SiH^{+}$. We believe that our value, *i.e.* 16.7 eV, is the correct one. The calculated vertical ionization energy amounts to 17.5 eV, 0.8 eV above the experimental one, which is still in modest agreement with the experimental number. If one would assume an adiabatic ionization of (**2**), the calculated energy would amount to $IE_{ad} = 16.5$ eV in good agreement with the experimental value. Analysis of the MIKE spectrum of SiH_2^{2+}, generated by 70 eV electron impact ionization of SiH_4, indicates that, in contrast to SiH^{2+}, only one stable SiH_2^{2+} ion is formed. The reaction $SiH_2^{2+} \longrightarrow SiH^{+} + H^{+}$ gives rise to one dished peak with $T_h = 3.06$ eV from which an intercharge distance of 4.74 Å can be calculated for the two departing monocations.

Like CH_3^{2+},[11] the open-shell dication SiH_3^{2+} is expected to be Jahn–Teller distorted from planar D_{3h} symmetry. Our geometry optimizations lead to two distinct C_{2v} structures of different electronic states (**4**) ($2A_1$) and (**5**) ($^2B_2$), (**4**) being more stable by 2.1 kcal mol^{-1}. The inspection of the force constant matrix shows one negative eigenvalue for (**5**), thus indicating this structure not to be a minimum on the potential energy surface. Structure (**4**) can be understood as a loosely bound complex of SiH_2^{2+} and H$^{\bullet}$ which is supported by a rather long (1.940 Å) and weak (Si–H stretch: 810 cm^{-1}) one-electron bond and the high spin density of 0.60 (6-31G**) at the weakly bound hydrogen. Furthermore, the geometry of the SiH_2 unit in (**4**) (Si–H bond length 1.477 Å, H–Si–H bond angle 160.1°) is quite similar to the isolated SiH_2^{2+} dication (**2**) (Si–H bond length 1.487 Å, H–Si–H bond angle 180.0°) and 86% of the positive charge is located on this moiety. From this theoretical result one would predict that SiH_3^{2+} is very unlikely to be observed as a stable species in the gas phase. Nevertheless, we found a signal corresponding to stable SiH_3^{2+}. Moreover, the comparison of the experimentally measured $Q_{min.}$ value, which is 15.4 eV and the calculated vertical ionization energy of 20.9 eV even increases the confusion. In order to check, whether also in this case an ionization involving the first excited state of SiH_3^{+} may play a role, we additionally computed the transition from the lowest $^3\Pi$ state of SiH_3^{+}. However, even this ionization requires 17.1 eV, still 1.7 eV above the experimental result. Better agreement would result if adiabatic ionization of the $^3\Pi$ state would occur for what a value of 15.9 eV can be extracted from the data given in Table 1. However, we are not certain whether charge stripping from SiH_3^{+} can be described within the simple picture of vertical *versus* adiabatic ionization, similar to the situation already encountered *e.g.* for CH_3OH^{+}[4a] and $C_2H_3O^{+}$.[4g] It should be mentioned that for the valence isoelectronic CH_3^{2+} dication the discrepancy of the calculated ionization energy and the $Q_{min.}$ value is also of the order of 5 eV, which should be beyond any experimental or computational uncertainties.[11] It is our firm belief that a reconciliation of the experimental and theoretical data can only be arrived at a more detailed understanding of the physics underlying the c.s. process.

For the higher silicon hydride dications no experimental data

Table 3. Deprotonation energies (kcal mol^{-1})

Molecule	Deprotonation energy^{a,b}
SiH_5^{2+}	−13.4
SiH_4^{2+}	−26.1
SiH_3^{2+}	−48.0
SiH_2^{2+}	−20.0
SiH^{2+}	−35.4
CH_4^{2+}	−105.7
CH_3^{2+}	−108.5
CH_2^{2+}	−71.4
CH^{2+}	−147.5

[a] Values for CH_n^{2+} are taken from ref. 11; calculated at MP4/6-311G**//6-31G*. [b] Values for SiH_n^+ are taken from 'The Carnegie-Mellon Quantum Chemistry Archive,' eds. R. A. Whiteside, M. J. Frisch, and J. A. Pople, Carnegie-Mellon University, Pittsburgh, 1983, 3rd edn.

are available due to the lack of the corresponding precursor monocations. Therefore, we will only briefly summarize the results of our calculations of these, until now hypothetical, dications.

While the only minimum found for CH_4^{2+} has a planar, D_{4h}, geometry,[11,16] the situation for SiH_4^{2+} is completely different. The corresponding D_{4h} SiH_4^{2+} has two negative eigenvalues of the Hessian matrix. However, for SiH_4^{2+} two different structures (**6**) and (**7**) are calculated as true minima, being 65.0 and 60.8 kcal mol^{-1} more stable than the quadratic structure, respectively. Both geometries can be interpreted as weakly bound complexes between H_2 and SiH_2^{2+}: structure (**6**) arises from the edge-on interaction of a hydrogen molecule with SiH_2^{2+}, whereas (**7**) is the end-on adduct. The donor–acceptor bonds connecting H_2 and SiH_2^{2+} are weak, which is revealed by the relatively long H_2–SiH_2 distance of 1.809 and 1.743 Å in (**6**) and (**7**), respectively.

The minimum structures found earlier for the SiH_5^+ monocation are complexes of the relatively stable SiH_3^+ cation and a hydrogen molecule, either in the edge-on, or in the end-on arrangement.[17] The loss of a further electron from SiH_5^+ is accompanied by only slight changes of these geometries. Our optimizations lead to the dications (**8**) and (**9**), which are adducts of H_2 and the SiH_3^{2+} dication (**4**). Among these two, (**8**) is by 5.5 kcal mol^{-1} more stable than (**9**). Since the SiH_3^{2+} dication, as mentioned above, is an adduct of an hydrogen atom and SiH_2^{2+}, the SiH_5^{2+} species have to be interpreted as weak complexes consisting of $H^{\bullet}$, H_2, and SiH_2^{2+}. Therefore, SiH_4^{2+} and SiH_5^{2+} should easily decompose, and it seems unlikely ever to observe them in the gas-phase experimentally.

Like all other small gas-phase dications, the SiH_n^{2+} species are thermodynamically highly unstable. However, their instabilities turn out to be less pronounced than for their carbon counterparts. This is clearly reflected by the calculated heats of reaction of the deprotonation reactions $SiH_n^{2+} \longrightarrow SiH_{n-1}^{+} + H^+$, which are much lower than those calculated for carbon[11] (Table 3). This is a direct consequence of the better capability of silicon to accommodate the positive charge which itself is certainly due to its lower electronegativity and its higher polarizability which are general features of second-row atoms compared with first row elements.

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