f polarization functions are added, $\alpha_0(d) = 0.20$ and $\alpha_0(f) = 0.61$, respectively. This basis set is contracted to [4s3p2d2f] using the ANO procedure. The two outermost s, p, and d primitive functions are uncontracted and a diffuse even-tempered s, p, and d function is added, resulting in a final basis set of the form (14s9p7d4f)/[7s6p5d2f]. This basis set yields a polarizability of 2.64 $a_0^3$, which is in good agreement with the recommended value (2.67 $a_0^3$) of Miller and Bederson.[30]

The Ar basis set is the larger (17s12p6d4f)/[8s7p4d2f] set employed in previous work.[6] This basis set yields a polarizability of 11.13 $a_0^3$, as compared with the recommended value of 11.10 $a_0^3$.[30]

## References and Notes

(1) Russell, D. H. Ed. *Gas Phase Inorganic Chemistry*; Plenum Press: New York, 1989.

(2) von Helden, G.; Kemper, P. R.; Bowers, M. T. *J. Chem. Phys.*, in press.

(3) Kemper, P. R.; Hsu, M.-T.; Bowers, M. T. *J. Phys. Chem.* **1991**, *95*, 10600.

(4) Lessen, D. E.; Asher, R. L.; Brucat, P. J. *Chem. Phys. Lett.* **1991**, *177*, 380.

(5) Almlöf, J.; Taylor, P. R. *J. Chem. Phys.* **1987**, *86*, 4070.

(6) Bauschlicher, C. W.; Partridge, H.; Langhoff, S. R. *J. Chem. Phys.* **1989**, *91*, 4733.

(7) Chong, D. P.; Langhoff, S. R. *J. Chem. Phys.* **1986**, *84*, 5606. See also: Ahlrichs, R.; Scharf, P.; Ehrhardt, C. *J. Chem. Phys.* **1985**, *82*, 890.

(8) Bauschlicher, C. W.; Langhoff, S. R.; Partridge, H.; Rice, J. R.; Komornicki, A. *J. Chem. Phys.* **1991**, *95*, 5142.

(9) Partridge, H.; Bauschlicher, C. W.; Pettersson, L. G. M.; McLean, A. D.; Liu, B.; Yoshimine, M.; Komornicki, A. *J. Chem. Phys.* **1990**, *92*, 5377.

(10) Bauschlicher, C. W.; Langhoff, S. R.; Taylor, P. R. *J. Chem. Phys.* **1988**, *88*, 2540.

(11) Partridge, H.; Bauschlicher, C. W.; Walch, S. P.; Liu, B. *J. Chem. Phys.* **1983**, *79*, 1866.

(12) Moore, C. E. *Atomic Energy Level*; National Bureau of Standards (US) Circ. 467 (1949).

(13) von Helden, G., personal communication.

(14) Lefebvre-Brion, H.; Field, R. W. *Perturbations in the Spectra of Diatomic Molecules*; Academic Press: Orlando, 1986.

(15) MOLECULE-SWEDEN is an electronic structure program system written by J. Almlöf, C. W. Bauschlicher, M. R. A. Blomberg, D. P. Chong, A. Heiberg, S. R. Langhoff, P.-Å. Malmqvist, A. P. Rendell, B. O. Roos, P. E. M. Siegbahn, and P. R. Taylor.

(16) Desclaux, P. *Atomic Data Nucl. Data Tables* **1973**, *12*, 312.

(17) Ahlrichs, R.; Böhm, H. H.; Brode, S.; Tang, K. T.; Toennies, J. P. *J. Chem. Phys.* **1988**, *88*, 6290.

(18) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(19) Bauschlicher, C. W.; Partridge, H. *J. Phys. Chem.* **1991**, *95*, 3946. Bauschlicher, C. W.; Partridge, H. *J. Phys. Chem.* **1991**, *96*, 9694.

(20) Lessen, D.; Brucat, P. J. *J. Chem. Phys.* **1989**, *90*, 6296.

(21) Lessen, D.; Brucat, P. J. *J. Chem. Phys.* **1989**, *91*, 4522.

(22) Lessen, D.; Brucat, P. J. *Chem. Phys. Lett.* **1988**, *152*, 473.

(23) Loh, S. K.; Fisher, E. R.; Lian, Li; Schultz, R. H.; Armentrout, P. B. *J. Phys. Chem.* **1989**, *93*, 3159.

(24) Bauschlicher, C. W.; Partridge, H.; Langhoff, S. R. *Chem. Phys. Lett.* **1990**, *165*, 272.

(25) Partridge, H. *J. Chem. Phys.* **1989**, *90*, 1043.

(26) Langhoff, S. R.; Partridge, H.; Bauschlicher, C. W. *Chem. Phys.* **1991**, *153*, 1.

(27) Partridge, H. *J. Chem. Phys.* **1987**, *87*, 6643.

(28) Reinsch, E.-A.; Meyer, W. *Phys. Rev.* **1976**, *A14*, 915.

(29) van Duijneveldt, F. B. *IBM Res. Rep.* **1971**, RJ 945.

(30) Miller, T. M.; Bederson, B. *Adv. Atom. Mol. Phys.* **1978**, *13*, 1.

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# Theoretical Study of the Thermochemical Stabilities of the Isomers of $[H_2,Si,O]^{\bullet+}$ in the Gas Phase[†]

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Ab initio MO calculations were performed on the potential energy surface of the $[H_2,Si,O]^{\bullet+}$ doublet state cations employing the UMP4SDTQ/6-31G**//UMP2/6-31G** + ZPVE approximation. The global minimum is found to correspond to the *trans*-hydroxysilylene isomer **2** ($HSiOH^{\bullet+}$). The cis isomer **2′** is 0.3 kcal mol$^{-1}$ higher in energy than **2**, and the transition structure TS **2/2′**, connecting the two conformers lies only 0.5 kcal mol$^{-1}$ above **2**. The association product of $Si^{\bullet+}$ with $H_2O$, i.e., $SiOH_2^{\bullet+}$ (**3**) is also a low-energy isomer being 3.8 kcal mol$^{-1}$ above **2**. A high barrier of 41.9 kcal mol$^{-1}$ (TS **2/3**) separates the two isomers. The fourth isomer, $H_2SiO^{\bullet+}$ (**1**), corresponding to the silicon analogue of ionized formaldehyde, also has a genuine minimum on the $[H_2,Si,O]^{\bullet+}$ potential energy surface. However, ionized silanone **1** lies 43.5 kcal mol$^{-1}$ above **2**. In addition, the barriers of **1** toward isomerization to **2** or dissociation to $H_2Si^{\bullet+}$ and an oxygen atom was relatively small. The MO calculations also provide insight into possible fragmentation mechanisms of $[H_2,Si,O]^{\bullet+}$ ions, and the relative bond-dissociation energies are discussed.

## Introduction

Small silicon-containing ions and corresponding neutral systems with the elementary composition $[H_2,Si,O]$ are receiving increasing attention, particularly in connection with ionospheric chemistry,[1] interstellar chemistry,[2,3] and plasma etching.[4-7] An understanding of the relevant silicon chemistry in these environments requires a knowledge of the thermodynamics of the individual processes. A further aspect of silicon species which has often been addressed in recent years and which is of fundamental interest from the point of view of theories of chemical bonding, concerns the character of multiple bonding to silicon. The Si–X *double* bond (when X is an element in the first row of the periodic table) is weaker than that with other elements in the same row because of the unfavorable overlap between the π-orbitals of Si and X (resulting from differences in size). The smaller Si–X bond energies, together with the differences in electronegativity which manifest themselves in higher bond polarities, are responsible for the higher reactivities of these species.

Considerable experimental and theoretical effort has gone into generating the individual neutral $[H_2,Si,O]$ isomers, proving their existence and determining their relative stability. For example, matrix isolation and gas-phase experiments have shown spectro-

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[†] Dedicated to Professor Hans-Friedrich Grützmacher, Bielefeld, on the occasion of his 60th birthday.

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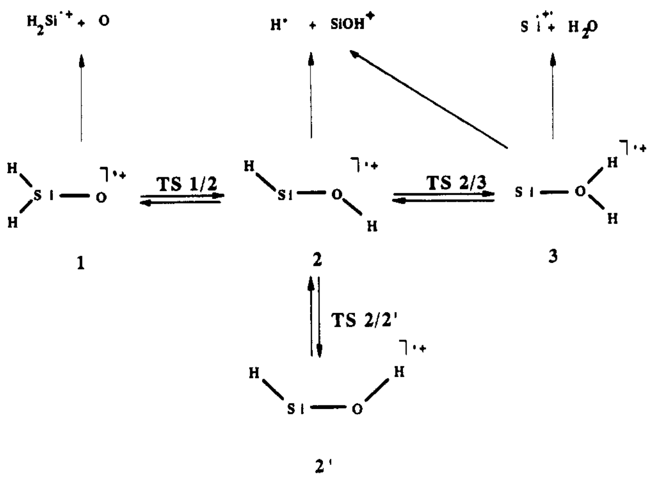
SCHEME I



scopically that silanone, $H_2SiO$, is a product of a reacting mixture of silane and ozone,[8,9] and that hydroxysilylene, HSiOH, arises from the adduct $SiOH_2$ formed in the reaction of atomic Si with $H_2O$.[10] High-level ab initio molecular orbital (MO) calculations which were performed concomitantly support the interpretation of these experimental results.[11-15] All of the investigations were restricted to neutral species. Other than ab initio MO calculations associated with a theoretical treatment of the kinetics of the reaction of $Si^{\cdot+}$ with $H_2O$[16] and an early study[17] on $SiOH_2^{\cdot+}$ no theoretical studies are known to us which were directed to a more detailed description of the potential energy surface (PES) of the corresponding $[H_2,Si,O]^{\cdot+}$ ions. Results are reported here for UMP4SDTQ/6-31G** ab initio calculations of the possible isomers for the $[H_2,Si,O]^{\cdot+}$ PES and also, at the same level, for transition structures (TS) and the dissociation energies of several exit channels. Scheme I provides an overview of the PES which was investigated. The calculations were performed in connection with our mass spectrometric experiments[18] which demonstrated the existence of the isomeric ions **1** and **2**/**2'** as well as the corresponding neutral species,[18] and in support of SIFT measurements of the reaction of $Si^{\cdot+}$ with $H_2O$.[16,19]

## Computational Details

All calculations were performed with the GAUSSIAN 90 program package[20] in the frame of the unrestricted Hartree–Fock formalism (UHF).[21] The geometry of the species which were examined were completely optimized (regardless of simplifications which may arise from symmetry) with the help of the analytically calculated first derivatives using the standard gradient procedure. All stationary points were rigorously characterized with regard to the number(s) of negative eigenvalues of the force constant matrix.

The designation 6-31G*//6-31G* is applied when the geometry was optimized with the polarized 6-31G* basis set,[22] which was also used to calculate the zero-point vibrational energies (ZPVEs). The values for ZPVE were scaled by a factor of 0.89 to compensate for the known systematic overestimation of the normal frequencies which result from the Hartree–Fock calculations.[23] The geometry of significant points on the PES was then reoptimized with a 6-31G** basis set,[24] including electron-correlation effects, with Møller–Plesset second-order (MP2) perturbation theory.[25] While some errors can result from the uncomplete treatment of the electron correlation, we assume that this will not constitute a serious problem at the UMP2 level.[25b,c] The final energies were then obtained using the geometries calculated in this way with a subsequent single-point post-SCF calculation at the UMP4 level and including single (S), double (D), triple (T) and quadruple (Q) excitation. These are designated as UMP4SDTQ/6-31G**//UMP2/6-31G**. These energies are then corrected for the ZPVE contributions calculated at UMP2/6-31G*, and we believe that these calculations should describe not only the geometric and electronic structure but also the relative stabilities with chemical accuracy.

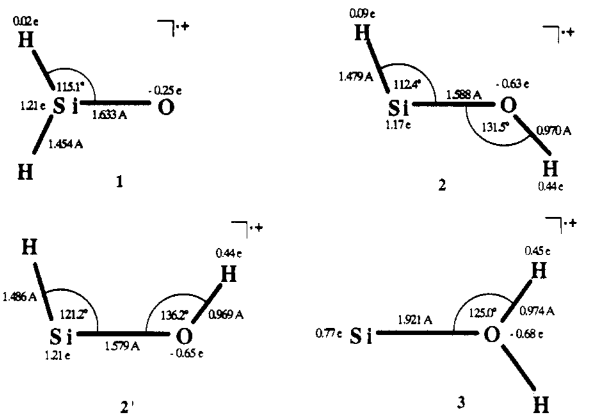


**Figure 1.** Equilibrium geometries for the four isomers of $[H_2,Si,O]^{\cdot+}$ calculated at the UMP2/6-31G**//UMP2/6-31G** level of theory and their charge distribution as derived from a Mulliken population analysis.

The UMP2/6-31G**//UMP2/6-31G** optimized geometries of the $[H_2,Si,O]^+$ isomers can be taken from the diagrams in the text. All bond lengths are given in angstroms and the angles in degrees. Also, unless stated otherwise in the text, the energies are given (in kcal $mol^{-1}$) at the UMP4SDTQ/6-31G**//UMP2/6-31G** level.

## Results and Discussion

**Equilibrium Structures.** Figure 1 shows the equilibrium geometries for the individual isomers **1**–**3** (Scheme I) calculated at the UMP2/6-31G**//UMP2/6-31G** level. As is the case with neutral silanone, the radical cation **1** is planar with a preferred $C_{2v}$ symmetry. The Si–O bond length is 1.633 Å and so considerably longer than that in the corresponding neutral (1.545 Å), but also longer (by 0.047 Å) than the Si–O single bond in the hydroxysilylene radical cation **2**. The Si–H bond is not very different than that in the isolated silene cation (1.461 Å).[26] The charge distribution from the Mulliken population analysis predicts a positive silicon atom ($q_{Si} = 1.21e$) while the spin is predicted to be localized on the oxygen atom. The calculated $^2A_1$ state of **1** is thus a "distonic"[27] ion. The formal separation of charge and spin density is reminiscent of the results of our calculations of $H_2SiCO^{\cdot+}$.[26]

Two isomers can be distinguished in the case of the hydroxysilylenes **2** (both $^2A'$ and $C_s$ symmetry). The bonding parameters of the trans conformation **2** are not very different from those of the cis conformer **2'**. For example, the Si–O bond lengths are only marginally different (1.586 Å for **2** vs 1.579 Å for **2'**), and the Si–H and O–H bonds are equivalent within the limits of tolerance of the approximation used in the calculations. However, significant differences are apparent in a comparison of the structures of the radical cations and their neutral counterparts. Ionization leads to contraction of both the Si–O bond (by ca. 0.100 Å) and the Si–H bond (by 0.38 Å) because of strong Coulombic attraction ($Q_O = -0.646e$). The strong Si–O $\pi$-overlap in both cases (**2** and **2'**) leads to a widening of the H–Si–O angle from 94.9° in neutral silanone[12b] to about 120° in the cations. The H–O–Si bond angle in the neutral is similarly increased from 112.1° to 131.5° and 136.2° in **2** and **2'**, respectively. The cationic and radical centers in **2** and **2'** are located on the Si atom, in contrast to **1**.

Structure **3**, which formally corresponds to an adduct of silicon and water, has a $^2B_2$ state with $C_{2v}$ symmetry. The structure is characterized by a large Si–O separation (1.921 Å), and an O–H bond which is only slightly different from that in the water molecule. The widening of the H–O–H angle from 103.9° to 125.0° reflects the perturbation of the $\pi$-population of the oxygen atom through the Si–O bond connection.

**Transition Structures and Their Harmonic Frequencies.** The transition structures (TS) connecting the isomers shown in Scheme I have been optimized at the UMP2/6-31G**//UMP2/6-31G** level. The resulting geometries together with the charge distributions are summarized in Figure 2 and the harmonic frequencies

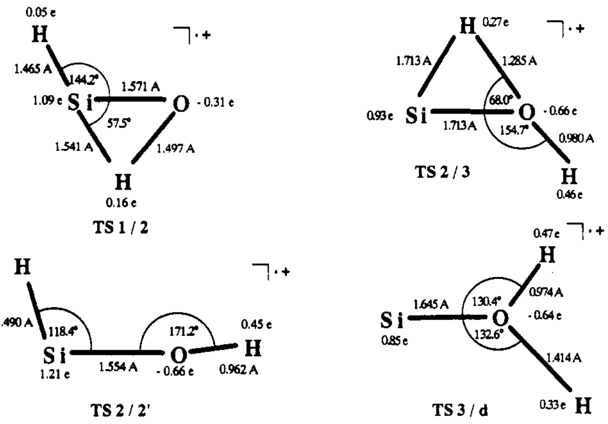


Figure 2. Transition structures (TS) for the interconversion of $[H_2,Si,O]^{\bullet+}$ calculated at the UMP2/6-31G**//UMP2/6-31G** level of theory and their charge distribution as derived from a Mulliken population analysis.

TABLE I: UMP2/6-31G**//UMP2/6-31G** Calculated Harmonic Frequencies ($cm^{-1}$) Scaled Due to the Overestimation of the Parabolic Approach by a Factor of 0.89 for the $[H_2,Si,O]^{\bullet+}$ Isomers and the Corresponding TS

| | |
|---|---|
| **1** (MIN) | 567 ($b_2$), 720 ($a_1$), 885 ($b_1$), 1016 ($a_1$), 2428 ($a_1$), 2501 ($b_2$) |
| **2** (MIN) | 531 (a′), 561 (a″), 689 (a′), 966 (a′), 2032 (a′), 3470 (a′) |
| **2′** (MIN) | 486 (a′), 492 (a″), 743 (a′), 1105 (a′), 2213 (a′), 3856 (a′) |
| **3** (MIN) | 375 ($b_1$), 426 ($a_1$), 607 ($b_2$), 1507 ($a_1$), 3353 ($a_1$), 3463 ($b_2$) |
| TS **1/2** | 479 (a″), 580 (a′), 1065 (a′), 2161 (a′), 2378 (a′) (−1778) |
| TS **2/2′** | 330 (a″), 737 (a′), 1157 (a′), 2167 (a′), 3955 (a′) (−395) |
| TS **2/3** | 153 (a″), 577 (a′), 801 (a′), 1536 (a′), 3290 (a′) (−1798) |
| TS **3/d** | 410 (a″), 569 (a′), 885 (a′), 1077 (a′), 3418 (a′) (−7984) |

are given in Table I. The transition structure TS **1/2** ($^2A'$) with $C_s$ symmetry corresponds to a 1,2 hydrogen migration having an imaginary frequency of $-1178$ $cm^{-1}$. This vibration is characteristic for such H-atom migrations, and the Si–H bond length (1.541 Å) corresponds to an elongation of this bond by approximately 10% which is what one normally assumes for such processes. The planarity of TS **1/2** is somewhat surprising in view of the findings by Kudo and Nagase[12b] for the neutral hydrosilylene $H_2SiO$ for which a nonplanar transition structure (torsion angle HSiO–H = 139.8°) for the 1,2 H shift was predicted at the UHF/6-31G* level. The results of our calculations on the radical cation of silanone, $H_2SiO^{\bullet+}$ (**1**) are more in line with the calculations of Schaefer et al.[28] on the isomerization of formaldehyde proceeding via planar transition structures. All of our attempts to locate a nonplanar transition structure for the reaction **1** $\rightleftarrows$ **2** up to the UMP2/6-31G**//UMP2/6-31G** level were unsuccessful. It should be mentioned that TS **1/2** found by us has one and only one imaginary frequency ($-1178$ $cm^{-1}$), and the out-of-plane H–Si–H bonding vibration has a positive frequency (479 $cm^{-1}$) supporting the planarity of the system.

The radical center in TS **1/2** is again located on the oxygen atom which explains the relatively long O–H separation (1.497 Å). The remaining bonding situations and the charge distributions largely correspond to that in structure **1**, thus pointing to an "early" transition structure.

The transition structure **2/3** with a negative frequency of $-1798$ $cm^{-1}$ corresponds to the closest saddle point in the consecutive transformation from **1** to **3** and fits well the transition structure in the neutral analogue (Si–O = 1.903 Å, Si–H = 1.721 A, O–H = 1.306 Å, ∠Si–O–H = 61.6°) calculated by Tachibana et al.[13b]

Another significant structure is TS **2/2′**, which corresponds to the barrier for the cis/trans isomerization. Again, we can only partially substantiate the results of the calculations by Kudo and Nagase for the neutral analogue.[12b] The structure with an imaginary frequency of $-394$ $cm^{-1}$ which we have calculated corresponds more to a hydrogen migration in plane (equivalent to an OH inversion) than an internal rotation. It seems that, in addition to the dependence of the results on the flexibility of the basis set which was determined by Kudo and Nagase,[12b] correlation effects also play a significant role for the geometry of the stationary points. This holds true in particular for transition structures.

TABLE II: Calculated Expectation Values $\langle S^2 \rangle$, Total Energies (hartrees), ZPVE[a] (in kcal/mol), and the Relative Stabilities[b] (kcal/mol) for the $[H_2,Si,O]^{\bullet+}$ Isomers

| | | $\langle S^2 \rangle$ | MP2[c] | MPV4[c] | ZPVE[a] | $\Delta E_r$[b] |
|---|---|---|---|---|---|---|
| **1** | ($^2A_1$) | 0.762 | −364.829 436 | −364.836 895 | 11.61 | 43.5 |
| **2** | ($^2A'$) | 0.760 | −364.906 148 | −364.913 641 | 13.87 | 0.0 |
| **2′** | ($^2A'$) | 0.760 | −364.902 199 | −364.909 122 | 11.31 | 0.3 |
| **3** | ($^2A_1$) | 0.766 | −364.899 910 | −364.911 540 | 16.33 | 3.8 |
| TS | **1/2** | 0.810 | −364.780 484 | −364.798 339 | 8.47 | 66.9 |
| TS | **2/2′** | 0.750 | −364.900 835 | −364.907 676 | 10.60 | 0.5 |
| TS | **2/3** | 0.762 | −364.815 552 | −364.841 652 | 10.61 | 41.9 |
| TS | **3/d** | 0.760 | −364.805 354 | −364.832 091 | 10.60 | 47.9 |

[a] Calculated frequencies scaled by 0.89. [b] $\Delta E_r$ relative stabilities based on the most stable isomer calculated from the scaled ZPVE corrected UMP4SDTQ/6-31G**//UMP2/6-31G** energies. [c] Total energies calculated at the UMP2/6-31G**//UMP2/6-31G** and UMP4SDTQ/6-31G**//UMP26-31G** level.

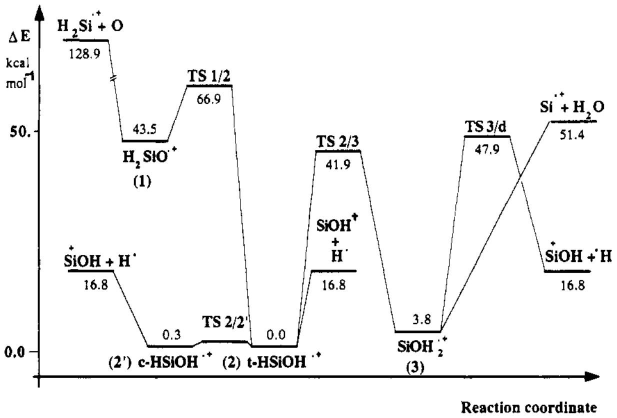


Figure 3. Total energy profile for the PES of $[H_2,Si,O]^{\bullet+}$ calculated at the UMP4SDTQ/6-31G**//UMP2/6-31** + ZPVE level of theory.

The last transition structure to be discussed in connection with the PES for $[H_2,Si,O]^{\bullet+}$ is the predissociative transition structure TS **3/d**. This structure is characterized by a high imaginary frequency of $-798.4$ $cm^{-1}$ and a lowering of the symmetry from $C_{2v}$ to $C_s$ relative to **3**. The two O–H bonds are no longer equivalent (O–H = 0.974 Å, O–H′ = 1.414 Å). The Si–O bond length of 1.645 Å is significantly shorter than that in **3** and is much closer to the bond length in $SiOH^+$ (1.556 Å). At the UMP2/6-31G**//UMP2/6-31G** level we could not locate transition structures for all of the other dissociation channels indicated in Scheme I.

**Energies.** The total energies calculated at the UMP4SDTQ/6-31G**/UMP2//6-31G** level and the values for the ZPVE are listed in Table II. In order to evaluate the possible contributions of higher spin contaminations, the computed expectation values $\langle S^2 \rangle$ are also included. Except for TS **1/2**, the values are close to a "pure" doublet state. The total energy profile for the PES of $[H_2,Si,O]^{\bullet+}$ is summarized in Figure 3. As mentioned in the Introduction, we are not aware of any other data available for comparison. Hopkinson and Lien[29] have calculated the hydroxysilylene cation, albeit at the UMP4SDTQ/6-31G**//UHF/6-31G** level, and obtained a structure very close to the structure (**2**) calculated by us but did not refer to the existence of further isomers nor to bond dissociation energies.

The most stable isomer on the $[H_2,Si,O]^{\bullet+}$ PES corresponds to structure *trans*-hydroxysilylene **2**. At the UMP4DTQ/6-31G**//UMP2/6-31G** level, the cis conformer **2′** lies only 2.8 kcal $mol^{-1}$ higher in energy and this difference disappears almost completely (0.3 kcal $mol^{-1}$) when corrected for ZPVE contributions. The two isomers are stabilized in the same way through $\pi$-donation into the empty 3p orbital of silicon. The electron deficiency of these silacations is partially compensated by the electron-rich donor (OH) which provides additional stabilization. A detailed discussion of this effect recently has been provided by Hopkinson and Lien.[29]

The barrier for cis/trans isomerization of 3.8 kcal mol$^{-1}$ is unusually small. The barrier for the neutral system was calculated to be 9.3 kcal mol$^{-1}$ at a similar level of theory (CISDQC/6-31G**//UHF/6-31G* + ZPVE).[12] We find this agreement satisfying since our experience has shown that the energy of the TS is very sensitive to the geometry and that the contribution of the correlation energy to the structure of similar systems must be regarded as significant.[26] The possible comparison with the calculation of Pople et al.[30] for the energy profile of the hypersurface of the carbon analogue $H_2CO$, which has a barrier ca. 30–35 kcal mol$^{-1}$ higher at the UMP4/6-31G**//UMP2/6-31G* level than that calculated by us for $[H_2,Si,O]^{\bullet+}$, is of limited value but may be used in a discussion of differences between silicon and carbon.

Structure **3** also lies in a deep energy minimum but is separated from the trans isomer **2** by a high barrier of 41.9 kcal mol$^{-1}$. As was the case with **2**, the high stability of **3** can be explained in terms of the interaction of the unoccupied 3p orbital of $Si^{\bullet+}(^2P)$ with the electron pair of water which gives rise to an enthalpy change of 49.3 kcal mol$^{-1}$ for the following reaction:

$$\underset{\mathbf{3}}{Si\text{–}OH_2^{\bullet+}} \rightarrow Si^{\bullet+}(^2P) + H_2O$$

As indicated in Figure 3, the O–H bond dissociation of $SiOH_2^{\bullet+}$ (**1**) via TS **3/d** competes with the isomerization process **3** → TS **2/3** → **2**. However, the energetics favor the latter reaction. In addition, the process **2** → $H^\bullet$ + $SiOH^+$ is barrier-free. Consequently, dissociation of **3** to generate $H^\bullet$ and $SiOH^+$ is predicted to proceed via a multistep path via **2** rather than involving TS **3/d**.

Structure **1**, $H_2SiO^{\bullet+}$, is the least stable of the $[H_2,Si,O]^{\bullet+}$ isomers. The minimum calculated for **1** lies 43.5 kcal mol$^{-1}$ higher in energy than that for the most stable structure **2**. This difference in energy is much less, 3.7 kcal mol$^{-1}$, for the neutral $H_2SiO$.[12b] The analysis of the wave function shows that the singly occupied molecular orbital primarily has the character of a SiH-$\sigma$ orbital and the removal of an electron has a destabilizing effect. From a chemical viewpoint, **1** corresponds formally to Si-protonated $HSiO^\bullet$, and it is evident that protonation on O, conditioned by the stabilization of the positive charge on the silicon, is preferred to the protonation of the electropositive Si center. The same effects have been found in studies of analogous Ge- and Se-bonded systems.[31,32]

## Conclusion

Structures **1**, **2**, **2′**, and **3** are equilibrium structures on the potential-energy hypersurface of $[H_2,Si,O]^{\bullet+}$ at the UMP2/6-31G**//UMP2/6-31G** level. They are found to be separated by significant energy barriers so that they should be stable and experimentally accessible to various entrance channels. These predictions are consistent with experimental results available to date. Charge-reversal experiments with the negative ions $[H_2,Si,O]^{\bullet-}$ generated from $C_6H_5SiH_3$ by chemical ionization in the presence of $N_2O$ have been reported which provide evidence for the connectivity **1**, $H_2SiO^{\bullet+}$.[18a] Evidence for the stability of **2**, $HSiOH^+$, has come from collisional activation and neutralization–reionization mass spectrometry of the ions $[H_2,Si,O]^{\bullet+}$ produced from electron impact of tetramethoxysilane.[18a] Selected-ion flow-tube experiments at room temperature and low pressure (0.35 Torr) of the reaction of $Si^{\bullet+}$ with $H_2O$ which correspond with structure **3**, $SiOH_2^{\bullet+}$, have shown the production of the bimolecular products $SiOH^+$ and $H^\bullet$ rather than stable $SiOH_2^{+}$.[19] The initial energy of the reactants is too high with respect to the height of the energy barrier and the probability of collisional stabilization is too low under these experimental conditions to allow formation of the $SiOH_2^{\bullet+}$ adduct ion. The reactions of $SiH_2^{\bullet+}$ with O and $SiOH^+$ with $H^\bullet$ which are possible sources of structures **1** and **2**, respectively, have not yet been experimentally investigated.

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## References and Notes

(1) Ferguson, E. E.; Fahey, D. W.; Fehsenfeld, F. C.; Albritton, D. L. *Planet. Space Sci.* **1975**, *23*, 1621.

(2) Turner, J. L.; Dalgarno, A. *Astrophys. J.* **1977**, *312*, 366.

(3) Herbst, E.; Millar, T. J.; Wlodek, S.; Bohme, D. K. *Astron. Astrophys.* **1989**, *222*, 205.

(4) Powell, M. J.; Easton, B. C.; Hill, O. F. *Appl. Phys. Lett.* **1981**, *38*, 794.

(5) Meiners, L. G. *J. Vac. Sci. Technol.* **1982**, *21*, 655.

(6) Lucuvsky, G.; Richard, P. D.; Tsu, D. V.; Lin, S. Y.; Markunas, R. J. *J. Vac. Sci. Technol.* **1986**, *A4*, 681.

(7) Kuschner, J. J. J. *Appl. Phys.* **1988**, *63*, 2532.

(8) (a) Withnall, R.; Andrews, L. *J. Phys. Chem.* **1985**, *89*, 3261. (b) Withnall, R.; Andrews, L. *J. Am. Chem. Soc.* **1985**, *107*, 2567.

(9) Ginski, R. J.; Gole, J. L.; Dixon, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 5891.

(10) Ismail, Z. K.; Hauge, R. H.; Frendin, L.; Kaufmann, J. W.; Margrave, J. L. *J. Phys. Chem.* **1982**, *77*, 1617.

(11) Jaquet, R.; Kutzelnigg, W.; Staemmler, V. *Theor. Chim. Acta* **1980**, *54*, 205.

(12) (a) Kudo, T.; Nagase, S. *J. Organomet. Chem.* **1983**, *253*, C23. (b) Kudo, T.; Nagase, S. *J. Phys. Chem.* **1984**, *88*, 2833. (c) Kudo, T.; Nagase, S. *J. Am. Chem. Soc.* **1985**, *107*, 2589.

(13) (a) Tashiba, A.; Fueno, H.; Yanabe, T. *J. Am. Chem. Soc.* **1986**, *108*, 4346. (b) Tachibana, A.; Koizumi, M.; Teramae, H.; Yanabe, T. *J. Am. Chem. Soc.* **1987**, *109*, 1383.

(14) Dixon, D. A.; Gole, J. L. *Chem. Phys. Lett.* **1986**, *125*, 179.

(15) Sauer, J.; Ahlrichs, R. J. *J. Chem. Phys.* **1990**, *93*, 2575.

(16) Wlodek, S.; Bohme, D. K.; Herbst, E. *Mon. Not. R. Astr. Soc.* **1990**, *242*, 674.

(17) Yanqui, T.; Berthier, G.; Panzat, F. *J. Mol. Sci.* **1984**, *2*, 1.

(18) (a) Srinivas, R.; Bohme, D. K.; Sülzle, D.; Schwarz, H. *J. Phys. Chem.* **1991**, *95*, 9836. (b) Srinivas, R.; Sülzle, D.; Koch, W.; DePuy, C. H.; Schwarz, H. *J. Am. Chem. Soc.* **1991**, *113*, 5970.

(19) (a) Wlodek, S.; Fox, A.; Bohme, D. K. *J. Am. Chem. Soc.* **1987**, *109*, 6603. (b) Bohme, D. K. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 719.

(20) GAUSSIAN 90: Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. Gaussian Inc.: Pittsburgh, PA.

(21) (a) Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* **1954**, *22*, 571. (b) Pople, J. A.; Raghavachari, K.; Frisch, M. J.; Binkley, J. S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1983**, *105*, 6389.

(22) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(23) Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Symp.* **1981**, *15*, 269.

(24) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(25) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum. Chem., Quantum Chem. Symp.* **1976**, *10*, 1. (c) Handy, N. C.; Knowles, P. J.; Samasundram, K. *Theor. Chim. Acta* **1985**, *68*, 87.

(26) Hrušák, J.; Srinivas, R.; Bohme, D. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1323.

(27) (a) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805. (b) Hammerum, S. *Mass Spectrom. Rev.* **1988**, *7*, 123.

(28) (a) Goddard, J. D.; Schaefer, H. F. *J. Chem. Phys.* **1979**, *70*, 5117. (b) Goddard, J. D.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1981**, *75*, 3459.

(29) Hopkinson, A. C.; Lien, M. H. *Can. J. Chem.* **1989**, *67*, 991.

(30) (a) Harding, L. B.; Schlegel, H. B.; Krishnan, R.; Pople, J. A. *J. Phys. Chem.* **1980**, *84*, 3394. (b) Frisch, M. J.; Krishnan, R.; Pople, J. A. *J. Phys. Chem.* **1981**, *85*, 1467.

(31) Antoniotti, P.; Grandinetti, F. *Gazz. Chim. Ital.* **1990**, *120*, 701.

(32) Grandinetti, F., private communication.