

IR Spectrum and Structure of a Protonated Disilane: Probing the Si–H–Si Proton Bridge**

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Although carbon and silicon are both group IV elements, their chemical bonding behavior is rather different. As Si–Si and Si–H bonds are weaker and less directional than C–C and C–H bonds, the bonding motifs in Si_nH_m show a much larger variety than their C_nH_m analogs. Si_nH_m often exhibit stable Si–H–Si bridges, which are rare for C_nH_m . In contrast to $\text{C}_n\text{H}_m^{(\pm)}$, $\text{Si}_n\text{H}_m^{(\pm)}$ are far less well-characterized because of the lack of suitable precursors. For example, although few SiH_m^+ ions were studied by IR spectroscopy,^[1] no spectroscopic data are available for Si_nH_m^+ with $n > 1$. In addition to theory of chemical bonding, Si_nH_m are interesting from a materials science point of view, as H passivation at the surface is predicted to turn reactive bare Si_n clusters into stable novel nanostructures with potential for technological applications.^[2] $\text{Si}_n\text{H}_m^{(\pm)}$ spectra are also required for comparison with astronomical data^[3] and diagnostics of silane plasmas used in the fabrication of microelectronic silicon-based devices.^[4] Here, we report the IR spectrum of disilanium, Si_2H_7^+ , a fully H-passivated Si_2 core with a Si–H–Si bridge described by a three-center two-electron (3c-2e) bond (Figure 1).

Almost no information is available for the Si_2H_7^+ cation. Early MP2/6-31G* calculations^[5] predict a D_{3d} symmetric global minimum with a linear $\text{H}_3\text{Si–H–SiH}_3$ proton bridge and a weakly bound $\text{Si}_2\text{H}_5^+\cdot\text{H}_2$ complex as local minimum, with stabilization energies of $D_0 = 146$ and about 38 kJ mol^{-1} , respectively. The Si_2H_7^+ cation dissociates barrierless into $\text{SiH}_3^+ + \text{SiH}_4$ with a measured binding energy greater than 146 kJ mol^{-1} .^[6] Binding of further SiH_4 ligands to SiH_3^+ is much weaker ($< 40 \text{ kJ mol}^{-1}$), suggesting that Si_2H_7^+ forms a stable core in $\text{SiH}_3^+\cdot(\text{SiH}_4)_n$ clusters.^[6] Although dissociation into $\text{Si}_2\text{H}_5^+ + \text{H}_2$ is less endothermic than into $\text{SiH}_3^+ + \text{SiH}_4$, it involves a high barrier lying slightly above the $\text{SiH}_3^+ + \text{SiH}_4$ limit.^[5,6]

The IR spectrum of Si_2H_7^+ is obtained by Ne-tagging IR photodissociation (IRPD) spectroscopy,^[7] a sensitive approach recently used to elucidate the structures of simple C_xH_y^+ ions^[8] and Si_2H_6^+ .^[9] $\text{Si}_2\text{H}_7^+\cdot\text{Ne}$ ions are generated in a supersonic plasma expansion containing SiH_4 and Ne. Due to the small $\text{Si}_2\text{H}_7^+\cdot\text{Ne}$ binding energy ($< 3 \text{ kJ mol}^{-1}$), the

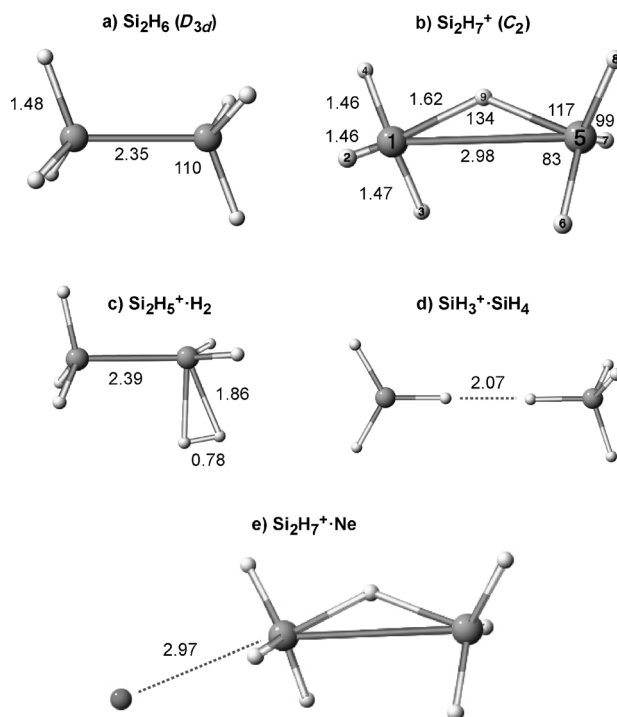


Figure 1. Structures of a) Si_2H_6 (D_{3d}), b) Si_2H_7^+ (C_2 , with atom numbering), c) $\text{Si}_2\text{H}_5^+\cdot\text{H}_2$, d) $\text{SiH}_3^+\cdot\text{SiH}_4$, and e) $\text{Si}_2\text{H}_7^+\cdot\text{Ne}$ calculated at the MP2/aug-cc-pVTZ level. Relevant structural parameters are given in ångströms and degrees (Table S1).

influence of Ne on the Si_2H_7^+ spectrum is negligible, and the single-photon IRPD spectrum of $\text{Si}_2\text{H}_7^+\cdot\text{Ne}$ (Figure 2) provides a close approximation to the IR spectrum of Si_2H_7^+ . All bands (A–E) in the $650\text{--}2200 \text{ cm}^{-1}$ range are assigned to fundamentals of the bridged $\text{H}_3\text{Si–H–SiH}_3$ ion.

MP2/aug-cc-pVTZ calculations elucidate the energetic, structural, electronic, and vibrational properties of Si_2H_6 , Si_2H_7^+ , and $\text{Si}_2\text{H}_7^+\cdot\text{Ne}$. The most stable structure of Si_2H_7^+ has a bent 3c-2e Si–H–Si bridge (Figure 1b). In contrast to all previous calculations at the MP2/6-31G* or lower levels,^[5] it has C_2 rather than D_{3d} symmetry. This structure can be generated either by protonation of the Si–Si single bond of Si_2H_6 or by addition of SiH_4 to SiH_3^+ . In the latter case, SiH_4 binds to the vacant electrophilic $3p_z$ orbital of SiH_3^+ in an orientation that allows for a weak Si–Si contact. Protonation of Si_2H_6 causes a drastic elongation of the Si–Si bond from 2.35 to 2.98 Å. The bent Si–H–Si bridge (134°) has long Si–H bonds (1.62 Å). The Si–H bonds of the SiH_3 groups contract upon protonation from 1.481 to about 1.465 Å, which is between those in SiH_3^+ (1.462 Å) and SiH_4 (1.478 Å). All

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[**] This study was supported by the Deutsche Forschungsgemeinschaft (grant numbers DO 729/5 and FOR 1282).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201208958>.

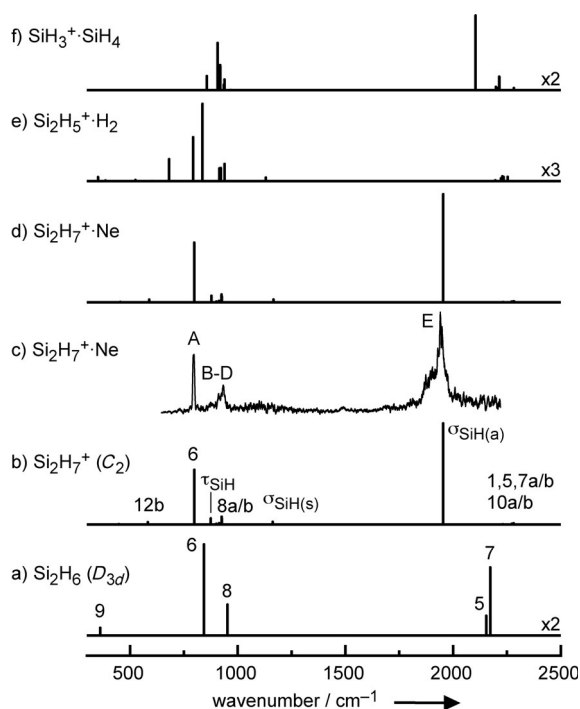


Figure 2. Experimental IRPD spectrum of c) $\text{Si}_2\text{H}_7^+\cdot\text{Ne}$ compared to the linear stick IR absorption spectra of a) Si_2H_6 (D_{3d}), b) Si_2H_7^+ (C_2), d) $\text{Si}_2\text{H}_7^+\cdot\text{Ne}$, e) $\text{Si}_2\text{H}_5^+\cdot\text{H}_2$, and f) $\text{SiH}_3^+\cdot\text{SiH}_4$ in their ground electronic states calculated at the MP2/aug-cc-pVTZ level (Figure 1). The positions and assignments of the observed transitions are listed in Table S2.

SiSiH bond angles deviate largely from the tetrahedral configuration in Si_2H_6 .

The natural bond orbital (NBO) charge distribution provides insight into the nature of the 3c-2e bond in Si_2H_7^+ (Figure 3). The charges $q_{\text{Si}} = 0.6$ and $q_{\text{H}} = -0.2$ e in Si_2H_6 are

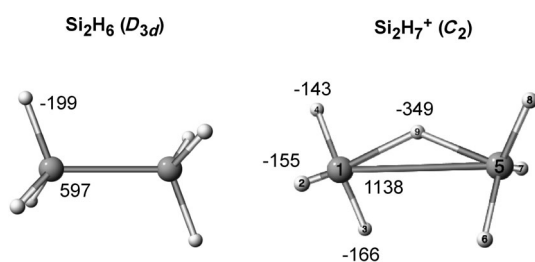


Figure 3. NBO charge distribution (in me) of Si_2H_6 (D_{3d}) and Si_2H_7^+ (C_2) evaluated at the MP2/aug-cc-pVTZ level.

consistent with the higher electronegativity of H than Si. In Si_2H_7^+ , both Si atoms absorb the excess positive charge ($q_{\text{Si}} = +1.14$ e), whereas all H atoms remain negative ($-q_{\text{H}} = 0.14$ – 0.35 e). Each SiH_3 unit in Si_2H_7^+ carries $+0.67$ e, that is, SiH_4 transfers formally 0.34 e into the $3p_z$ orbital of SiH_3^+ . In the limit of ionic bonding, Si_2H_7^+ can be described as $\text{H}_3\text{Si}^+-\text{H}^--\text{SiH}_3^+$. Hence, Si_2H_7^+ is rather different from N_2H_7^+ and O_2H_5^+ , which in the ionic limit are proton-bound complexes, $\text{H}_3\text{N}-\text{H}^+-\text{NH}_3$ and $\text{H}_2\text{O}-\text{H}^+-\text{OH}_2$.^[10] This view of

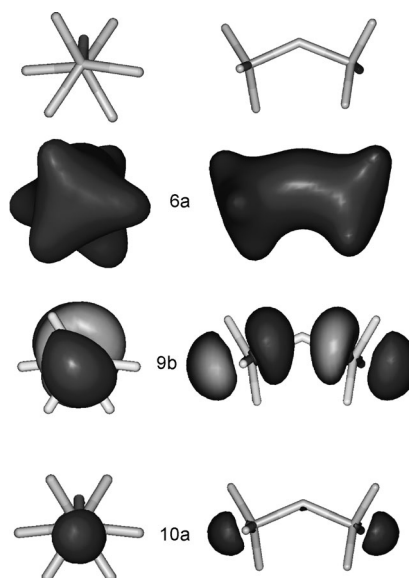


Figure 4. Front and side views of the three molecular orbitals of the 3c-2e bond in Si_2H_7^+ (C_2). The occupied 6a orbital is the bonding MO, whereas the vacant 9b and 10a orbitals are antibonding MOs.

bonding in Si_2H_7^+ is confirmed by the molecular orbitals (MOs) of its ^1A ground-state configuration, $[\text{NeNe}](6a)^2(6b)^2(7a)^2(8a)^2(7b)^2(9a)^2(8b)^2$. The three MOs of the 3c-2e bond^[11] in Figure 4 are the bonding 6a MO, which is delocalized over the whole Si_2H_7^+ ion, and the two vacant antibonding 9b and 10a MOs. All other occupied valence MOs are localized on the SiH_3^+ fragments and do not contribute to the 3c-2e bond (see Figure S1 in the Supporting Information).

The proton affinity of Si_2H_6 has not been measured. The calculated protonation energy for the C_2 structure ($E_0 = 745$ kJ mol⁻¹) is much larger than that measured for C_2H_6 (596 kJ mol⁻¹),^[12] indicating that protonation of a polysilane Si–Si single bond is more exothermic than protonation of an alkane C–C bond. Collisional activation of Si_2H_7^+ produces SiH_3^+ as major fragment ion (loss of SiH_4 , Figure S2). Minor Si_2H_5^+ and Si_2H_3^+ ions arise from sequential H_2 loss. This fragmentation pattern is at first glance surprising, as H_2 loss is predicted as lowest fragment channel ($D_0 = 107$ kJ mol⁻¹), whereas SiH_4 loss requires 148 kJ mol⁻¹. The latter value agrees with the lower experimental limit of 146 kJ mol⁻¹.^[6] The minor observation of H_2 loss is due to a barrier higher than the limit for barrierless SiH_4 loss.^[5]

In addition to the global minimum of Si_2H_7^+ (C_2), the potential reveals further low-energy stationary points within 5 kJ mol⁻¹. These Si_2H_7^+ structures with C_s , C_{2v} , D_{3d} , and D_{3h} symmetries (Figure S3 and Tables S3 and S4) are first- or higher-order transition states (TS_n , $n = 1$ – 3) for interconversion of equivalent global minima through SiH_3 rotation and motion of the central proton around or perpendicular to the Si–Si bond. The C_s (C_{2v}) structures at $+0.05$ ($+2.5$) kJ mol⁻¹ are TS_1 with staggered (eclipsed) geometries with planar H–Si–H–Si–H configurations obtained by rotation of the excess proton and the SiH_3 groups around the Si–Si axis (Figure S4). They have similar Si–Si and Si–H bond lengths as

the C_2 structure. The D_{3d} (D_{3h}) structures at +3.7 (+4.3) kJ mol⁻¹ are derived from the C_{2v} and C_s structures as TS2 (TS3) by pushing the excess proton in the linear Si–H–Si configuration. They have slightly longer Si–Si distances and the Si–H bonds of the bridge contract substantially. Scrambling of the SiH₃ protons in Si₂H₇⁺ occurs by low internal rotation barriers through the C_s and C_{2v} structures ($V_b < 3$ kJ mol⁻¹), whereas scrambling of the central and terminal protons by a SiH₃⁺–SiH₄ transition state (C_s) requires much more energy ($V_b = 64$ kJ mol⁻¹). Only calculations at the correlated level using extended basis sets properly reproduce the bent Si–H–Si bridge.

In addition to the five low-energy Si₂H₇⁺ structures with the 3c-2e bond, there are stable high-energy Si₂H₅⁺·H₂ and SiH₃⁺·SiH₄ complexes on the Si₂H₇⁺ potential. In Si₂H₅⁺·H₂ (Figure 1c), H₂ binds weakly to the 3p_z orbital of a classical H₃Si–SiH₂⁺ ion with $D_0 = 41$ kJ mol⁻¹. The SiH₃⁺·SiH₄ structure in Figure 1d has a weak dihydrogen bond with $D_0 = 9.5$ kJ mol⁻¹, H₂SiH⁺–HSiH₃, which is typical for X–H–H–Y contacts in which X or Y are more electropositive than H.^[13]

To assign the experimental Si₂H₇⁺·Ne spectrum, linear IR absorption spectra are compared for the various Si₂H₇⁺ minima in Figure 2, namely Si₂H₇⁺ (C_2), Si₂H₅⁺·H₂, and SiH₃⁺·SiH₄. To judge the effects of protonation and complex formation, calculated IR spectra of Si₂H₆, Si₂H₅⁺, SiH₃⁺, and SiH₄ are presented in Figure 2 and Figure S5. Comparison of the IR spectra of Si₂H₇⁺ with C_2 , C_s , C_{2v} , D_{3d} , and D_{3h} symmetries unravels the effects of SiH₃ rotation and motion of the central proton on the IR spectrum (Figure S5). All 12 fundamentals of Si₂H₆ (¹A_{1g}, D_{3d}), ν_{1-12} , are known.^[14] They transform as $\Gamma_{\text{vib}} = 3a_{1g} + a_{1u} + 2a_{2u} + 3e_u + 3e_g$. The a_{2u} ($\nu_{5/6}$) and e_u (ν_{7-9}) modes are IR active. Protonation of Si₂H₆ reduces the symmetry from D_{3d} to C_2 , leading to $\Gamma_{\text{vib}} = 11a + 10b$. As a result, all Si₂H₇⁺ modes become IR active and all e modes split into a/b doublets. The Si–H stretch frequencies of the SiH₃ groups ($\nu_{1,5,7,10}$) increase by 68–109 cm⁻¹ (3–5 %) as a result of the Si–H bond contraction upon protonation and thus shift outside the spectral range investigated. As their IR intensities are reduced by 1–2 orders of magnitude, they would not have been observed in the experimental spectrum at the current sensitivity. The Si–Si stretch frequency (ν_3) decreases by a factor three from 430 to 150 cm⁻¹ as a result of proton insertion. The SiH₃ torsional frequency (ν_4) decreases slightly from 137 to 119 cm⁻¹, in line with a lower barrier for internal rotation calculated for the protonated species (210 vs. 347 cm⁻¹).^[9] The frequency of the IR-active asymmetric SiH₃ deformation decreases by about 27 cm⁻¹ and both components ($\nu_{8a,b}$) remain strongly IR active. Similarly, the anti-symmetric SiH₃ umbrella frequency (ν_6) appears with reduced frequency (–44 cm⁻¹) as a prominent transition in the IR spectrum of Si₂H₇⁺. The frequencies of the degenerate symmetric and antisymmetric SiH₃ rocking modes ($\nu_{9,12}$) exhibit large splittings upon protonation (560 and 135 cm⁻¹), and their center frequencies are substantially reduced (by 35 and 111 cm⁻¹). Due to their low IR intensity, they are not observed in the measured IR spectrum. The excess proton in the Si–H–Si bridge generates three additional fundamentals (Figure S6), and their significant IR intensities provide the

fingerprint of the 3c-2e bond. The asymmetric Si–H stretch mode has a rather low frequency because of the long Si–H bonds and dominates the predicted IR spectrum ($\sigma_{\text{SiH(a)}} = 1954$ cm⁻¹, $I = 1261$ km mol⁻¹). The torsional mode of the proton around the Si–Si bond and the symmetric Si–H stretch mode are predicted with medium IR intensity at $\tau_{\text{SiH}} = 875$ and $\sigma_{\text{SiH(s)}} = 1163$ cm⁻¹. In contrast to all other IR intense modes, $\sigma_{\text{SiH(s)}}$ is drastically affected by anharmonicity, which shifts its frequency from 1163 into the 500–700 cm⁻¹ range (Figure S7 and Table S5).

To estimate the effects of Ne tagging on the structure and IR spectrum of Si₂H₇⁺, stable Si₂H₇⁺·Ne complexes have been calculated. In the most stable one (Figure 1e), Ne binds to one of the SiH₃ groups with $D_0 = 2.6$ kJ mol⁻¹ at a Ne–Si separation of 2.97 Å.^[9] The by far largest effects on the Si₂H₇⁺ geometry upon asymmetric Ne complexation are a slight contraction of the Si–Si bond (1 mÅ) and an asymmetric elongation/contraction of the Si–H bonds in the 3c-2e bond (± 3 mÅ). All other bond lengths and angles change less than 1 mÅ and 1°. Except for ν_{9b} , all frequencies are affected by less than 10 cm⁻¹ and the IR intensities also show only minor changes. The negligible effects of Ne on the Si₂H₇⁺ spectrum is not only confirmed by the calculation but also by the similarity of the experimental Si₂H₇⁺·Ne and Si₂H₇⁺·Ar spectra (Figure S8).

Figure 2 reveals a good match between the IRPD spectrum measured for Si₂H₇⁺·Ne and the IR spectra calculated for Si₂H₇⁺·Ne and Si₂H₇⁺ with C_2 symmetry. The bands A–E at 795, 875, 911, 933, and 1941 cm⁻¹ are assigned to ν_6 , τ_{SiH} , ν_{8b} , ν_{8a} , and $\sigma_{\text{SiH(a)}}$, respectively, and the deviation between measured and calculated frequencies is less than 15 cm⁻¹. All transitions with predicted intensities $I > 50$ km mol⁻¹ are observed. The measured Si₂H₇⁺·Ne spectrum deviates largely from those predicted for Si₂H₅⁺·H₂ and SiH₃⁺·SiH₄, confirming that the observed Si₂H₇⁺ ion has indeed the 3c-2e bond. Bands A–D have widths of about 10 cm⁻¹, consistent with unresolved rotational structure. Band E assigned to $\sigma_{\text{SiH(a)}}$ exhibits a much larger width of about 120 cm⁻¹ and a pronounced substructure. As the Si₂H₇⁺·Ar spectrum shows the same phenomenon, the large width of the $\sigma_{\text{SiH(a)}}$ band is attributed to the high fluxionality of the central proton moving in a flat potential perpendicular to the Si–Si axis. Comparison of the IR spectra calculated for the bent and linear structures of Si₂H₇⁺ (Figure S5) reveals that the $\sigma_{\text{SiH(a)}}$ frequency is particularly sensitive to the proton position, confirming that the structure of the $\sigma_{\text{SiH(a)}}$ band provides a sensitive probe of the floppy Si–H–Si 3c-2e bond.

In conclusion, Ne-tagging IRPD spectroscopy provides the first spectroscopic and structural characterization of the Si₂H₇⁺ cation. Analysis of its IR spectrum unravels details of the Si–Si and Si–H bond properties in this fundamental polysilane cation featuring a bent but fluxional 3c-2e bond. The spectrum provides benchmark data for dynamical simulations^[15] of the effects of the low-barrier proton and SiH₃ motions on the vibrational and electronic properties of this fundamental type of Si–H–Si bond. The combined experimental and quantum chemical approach is suitable for the largely unexplored vibrational and electronic spectroscopy of Si_nH_m[±] ions and their clusters. Future directions

include the effects of functional groups, hybrid formation, ligand adsorption, and doping of $\text{Si}_n\text{H}_m^\pm$ with heteroatoms to modify the geometric and electronic properties these fundamental silicon species.

Experimental Section

IRPD spectra of $\text{Si}_2\text{H}_7^+\text{Ne}$ were recorded in a tandem quadrupole mass spectrometer (QMS1/2).^[16] $\text{Si}_2\text{H}_7^+\text{Ne}$ clusters were generated in a pulsed supersonic plasma beam expansion of a $\text{SiH}_4/\text{He}/\text{Ne}$ gas mixture (ratio 1:20:300) at 16 bar stagnation pressure. Weakly bound $\text{Si}_2\text{H}_7^+\text{Ne}$ ions were produced by electron and chemical ionization of SiH_4 and subsequent three-body aggregation. The composition of Si_2H_7^+ and $\text{Si}_2\text{H}_7^+\text{Ne}$ was confirmed by collision-induced dissociation (Figure S2). $\text{Si}_2\text{H}_7^{+,20}\text{Ne}$ ions were mass-selected by QMS1 and irradiated in an octopole with a tuneable IR laser pulse (ν_{IR}). Resonant vibrational excitation of $\text{Si}_2\text{H}_7^+\text{Ne}$ induced the rupture of the weak intermolecular bond. Resulting Si_2H_7^+ fragments were selected by QMS2 and monitored as a function of ν_{IR} to obtain IRPD spectra of $\text{Si}_2\text{H}_7^+\text{Ne}$. The IRPD yield was normalized for laser intensity variations measured with a pyroelectric detector. Calculations were carried out at the MP2/aug-cc-pVTZ level.^[17] Relative energies (E_{e}) and binding energies (D_{e}) were corrected for zero-point vibrational energies to derive E_0 and D_0 . Harmonic frequencies are scaled by factors of 0.9518 (0.9742) for frequencies above (below) 1500 cm^{-1} to optimize the agreement between calculated and measured frequencies of Si_2H_6 .^[9]

Received: November 9, 2012

Published online: December 20, 2012

Keywords: Gas-phase chemistry · IR spectroscopy · protonated disilane · silicon · structure elucidation

- [1] a) D. M. Smith, P. M. Martineau, P. B. Davies, *J. Chem. Phys.* **1992**, 96, 1741; b) D. W. Boo, Y. T. Lee, *J. Chem. Phys.* **1995**, 103, 514; c) Y. B. Cao, J. H. Choi, B. M. Haas, M. S. Johnson, M. Okumura, *J. Phys. Chem.* **1993**, 97, 5215.
- [2] a) J. Fischer, J. Baumgartner, C. Marschner, *Science* **2005**, 310, 825; b) R. Singh, *J. Phys. Condens. Matter* **2008**, 20, 045226; c) V. Kumar, Y. Kawazoe, *Phys. Rev. Lett.* **2003**, 90, 055502; d) R. D. Miller, J. Michl, *Chem. Rev.* **1989**, 89, 1359.
- [3] a) M. C. McCarthy, C. A. Gottlieb, P. Thaddeus, *Mol. Phys.* **2003**, 101, 697; b) R. I. Kaiser, Y. Osamura, *Astron. Astrophys.* **2005**, 432, 559.
- [4] a) M. J. Kushner, *J. Appl. Phys.* **1988**, 63, 2532; b) M. L. Mandich, W. D. Reents, M. F. Jarrold, *J. Chem. Phys.* **1988**, 88, 1703.
- [5] a) K. Raghavachari, *J. Chem. Phys.* **1990**, 92, 452; b) L. A. Curtiss, K. Raghavachari, P. W. Deutsch, J. A. Pople, *J. Chem. Phys.* **1991**, 95, 2433.
- [6] K. Hiraoka, J. Katsuragawa, A. Minamitsu, *Chem. Phys. Lett.* **1997**, 267, 580.
- [7] L. I. Yeh, M. Okumura, J. D. Myers, J. M. Price, Y. T. Lee, *J. Chem. Phys.* **1989**, 91, 7319.
- [8] a) G. E. Douberly, A. M. Ricks, B. W. Ticknor, P. V. R. Schleyer, M. A. Duncan, *J. Am. Chem. Soc.* **2007**, 129, 13782; b) G. E. Douberly, A. M. Ricks, P. V. R. Schleyer, M. A. Duncan, *J. Chem. Phys.* **2008**, 128, 021102; c) A. M. Ricks, G. E. Douberly, P. V. R. Schleyer, M. A. Duncan, *Chem. Phys. Lett.* **2009**, 480, 17; d) A. M. Ricks, G. E. Douberly, P. V. Schleyer, M. A. Duncan, *J. Chem. Phys.* **2010**, 132, 051101; e) H. S. Andrei, N. Solca, O. Dopfer, *Angew. Chem.* **2008**, 120, 401; *Angew. Chem. Int. Ed.* **2008**, 47, 395; f) O. Dopfer, D. Roth, J. P. Maier, *J. Am. Chem. Soc.* **2002**, 124, 494; g) H. S. Andrei, S. A. Nizkorodov, O. Dopfer, *Angew. Chem.* **2007**, 119, 4838; *Angew. Chem. Int. Ed.* **2007**, 46, 4754; h) A. Patzer, S. Chakraborty, N. Solca, O. Dopfer, *Angew. Chem.* **2010**, 122, 10343; *Angew. Chem. Int. Ed.* **2010**, 49, 10145; i) N. Solcà, O. Dopfer, *Angew. Chem.* **2002**, 114, 3781; *Angew. Chem. Int. Ed.* **2002**, 41, 3628; j) A. Patzer, M. Schütz, T. Möller, O. Dopfer, *Angew. Chem.* **2012**, 124, 5009; *Angew. Chem. Int. Ed.* **2012**, 51, 4925; k) M.-E. Crestoni, S. Fornarini, *Angew. Chem.* **2012**, 124, 7487; *Angew. Chem. Int. Ed.* **2012**, 51, 7373.
- [9] M. Savoca, M. A. R. George, J. Langer, O. Dopfer, *Phys. Chem. Chem. Phys.*, DOI: 10.1039/c2cp43773b.
- [10] The NBO charges for the proton in the symmetric X–H–X bonds are -0.42 , $+0.46$, and $+0.58\text{ e}$ in $[\text{H}_3\text{Si}-\text{H}-\text{SiH}_3]^+$, $[\text{H}_3\text{N}-\text{H}-\text{NH}_3]^+$, and $[\text{H}_2\text{O}-\text{H}-\text{OH}_2]^+$.
- [11] a) R. L. Dekock, W. B. Bosma, *J. Chem. Educ.* **1988**, 65, 194; b) J. E. McMurry, T. Lectka, *Acc. Chem. Res.* **1992**, 25, 47.
- [12] E. P. L. Hunter, S. G. Lias, *J. Phys. Chem. Ref. Data* **1998**, 27, 413.
- [13] a) G. N. Patwari, T. Ebata, N. Mikami, *J. Chem. Phys.* **2000**, 113, 9885; b) R. Custelcean, J. E. Jackson, *Chem. Rev.* **2001**, 101, 1963.
- [14] a) G. W. Bethke, M. K. Wilson, *J. Chem. Phys.* **1957**, 26, 1107; b) J. R. Durig, J. S. Church, *J. Chem. Phys.* **1980**, 73, 4784; c) N. Moazzen-Ahmadi, V. M. Horneman, *J. Chem. Phys.* **2006**, 124, 194309.
- [15] a) O. Vendrell, F. Gatti, H. D. Meyer, *Angew. Chem.* **2009**, 121, 358; *Angew. Chem. Int. Ed.* **2009**, 48, 352; b) S. D. Ivanov, O. Asvany, A. Witt, E. Hugo, G. Mathias, B. Redlich, D. Marx, S. Schlemmer, *Nat. Chem.* **2010**, 2, 298; c) K. R. Asmis, Y. G. Yang, G. Santambrogio, M. Brummer, J. R. Roscioli, L. R. McCunn, M. A. Johnson, O. Kuhn, *Angew. Chem.* **2007**, 119, 8846; *Angew. Chem. Int. Ed.* **2007**, 46, 8691.
- [16] a) O. Dopfer, *Int. Rev. Phys. Chem.* **2003**, 22, 437; b) O. Dopfer, *Z. Phys. Chem.* **2005**, 219, 125; c) E. J. Bieske, O. Dopfer, *Chem. Rev.* **2000**, 100, 3963.
- [17] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09 Rev. A.02, Gaussian Inc., Wallingford CT, **2009**.