Ring-Opening Vibrations of Spherosiloxanes

Peter Bornhauser and Gion Calzaferri*

Institute for Inorganic and Physical Chemistry, University of Berne, Freiestrasse 3, CH-3000 Bern 9, Switzerland

Received: August 2, 1995; In Final Form: October 24, 1995

The ring-opening vibrations of the spherolasesquioxanes of the general formula (HSiO_{3/2})_n, n = 2, 3, 4, etc., are normal modes in which all Si–O stretching and/or O–Si–O bending displacements of the considered ring are in phase. We have investigated the vibrational structure of the experimentally well-known H_8Si_8O_{15} and H_{10}Si_{10}O_{15} and of I_6-H_20Si_{20}O_{30} and O_6-H_22Si_{12}O_{36}, which are not yet known as isolated molecules. The energy range of the 11 IR active, the 15 Raman active, and the three inactive ring-opening modes which belong to the 4-, 5-, and 6-ring vibrations of O_6-H_8Si_8O_{12}, D_{5h}-H_{10}Si_{10}O_{15}, I_6-H_20Si_{20}O_{30}, and O_6-H_22Si_{12}O_{36} decreases from 490–390 to 440–250 to 340–219 cm\(^{-1}\). The 4-, 5-, and 6-rings are in fact built of four, five, and six Si atoms plus four, five, and six O atoms, respectively. The totally symmetric vibrations show predominantly stretching character with one exception, the \(\delta(O–Si–O)\) line at 451 cm\(^{-1}\) of H_{22}Si_{12}O_{36}. They occur in specific regions, namely, at 460–440 cm\(^{-1}\) for the 4-ring, at 340–250 cm\(^{-1}\) for the 5-ring, and at 220–210 cm\(^{-1}\) for the 6-ring. We show that the ring-opening vibrations of the hydrosilasesquioxanes suggest a new way to study the pore-opening vibrations of zeolites, which simplifies the problem remarkably and thus leads to a better understanding of the more complex extended structures. The vibrations of the investigated spherosiloxanes can be divided into six distinct regions denoted as \(\nu(Si–H), \nu_a(Si–O–Si), \delta(O–Si–O), \delta(Si–O–Si)\). This means that the concept of group frequencies makes sense. However 10 modes were observed which do not fit into this general scheme, namely, the modes at 481 and 446 cm\(^{-1}\) (H_8Si_8O_{12}), at 455, 450, and 334 cm\(^{-1}\) (H_{10}Si_{10}O_{15}), at 336, 284, and 251 cm\(^{-1}\) (H_{22}Si_{12}O_{36}), and at 219 and 214 cm\(^{-1}\) (H_{24}Si_{24}O_{36}). All of them can be identified as ring-opening vibrations.

I. Introduction

The cage-shaped hydrosilasesquioxanes of the general formula (HSiO_{3/2})_n, n = 2, 3, etc., are appealing molecules for studying structural, electronic, and vibrational properties of silicon dioxide cage structures. Some of them may be considered as molecular models of the building units found in infinitely extended zeolite and silicate frameworks. The crystal structures of H_8Si_8O_{12}, H_{10}Si_{10}O_{15}, and H_{12}Si_{12}O_{18} were studied in detail, and those of the two isomers of H_{14}Si_{14}O_{16} were reported. These molecules have recently been discussed as precursors for atomic scale control of the Si/SiO_2 interface. H_8Si_8O_{12} has shown to be a suitable starting molecule to synthesize mono substitutes octanuclear silasesquioxanes. Its electronic structure and the Si–H + Y–Z → Si–Y + H–Z reaction mechanism under retention of the cage have been studied. Some of the R_8Si_8O_{12} molecules have been discussed as building blocks for the preparation of highly silicic materials or as starting molecules for new organosilicic materials. Amazingly, stable encapsulation of atomic hydrogen upon \(\gamma\)-irradiation of [(CH_3)_3SiO]_8Si_8O_{12} was reported recently.

We measured and analyzed the IR, the FT-Raman, and the INS spectra of H_8Si_8O_{12} in detail, and the correlation between idealized D_{4h} oligomeric (HSiO_{3/2})_n (n = 3, 4, 5, and 6) was reported in a preliminary communication. It was shown that the force field determined for H_8Si_8O_{12} is appropriate to describe the fundamentals of H_{10}Si_{10}O_{15}. When carrying out this work, we observed that these molecules are suited as models for studying pore-opening vibrations, which are believed to play an important role in the dynamics and the transport properties of zeolites. We explain this for O_6-H_8Si_8O_{12}, D_{5h}-H_{10}Si_{10}O_{15}, I_6-H_20Si_{20}O_{30}, and O_6-H_22Si_{12}O_{36}. Their geometry is illustrated in Scheme 1. The corners represent the positions of the Si atoms, while the bridging oxygen and the terminal hydrogen atoms are not shown. I_6-H_20Si_{20}O_{30} and O_6-H_22Si_{12}O_{36} are not yet known as isolated molecules. We introduce the ring-opening vibrations as normal modes in which all Si–O stretching and/or O–Si–O bending displacements of the considered ring are in phase, and we analyze their properties for the 4-, 5-, and 6-rings, which in fact are built of four, five, and six Si atoms plus four, five, and six O atoms, respectively.

The aluminosilicate framework of zeolite A can be built of double 4-rings (D4R) connected by oxygen bridges. A detailed comparison between silasesquioxane molecules and LTA zeolites was presented recently. We described H_8Si_8O_{12}...
as a model for the vibrational structure of zeolite A.\textsuperscript{14} A consequence of these ideas is shown in Scheme 2, in which the hydrosilasesquioxanes \( \text{H}_8\text{Si}_8\text{O}_{12} \) and \( \text{H}_{24}\text{Si}_{24}\text{O}_{36} \) are related to the structure of zeolite A. Since \( \text{H}_{24}\text{Si}_{24}\text{O}_{36} \) bears the structure of the sodalite cage, it may be used as a link to the many zeolites in which this structure is present.\textsuperscript{19} A similar link to clathrasils\textsuperscript{20} can be tried via the \( \text{H}_{20}\text{Si}_{20}\text{O}_{30} \). Several attempts have been made to assign the observed vibrational modes to specific local structural features of zeolites and especially to pore-opening vibrations.\textsuperscript{21–27} We now show that the ring-opening vibrations of the hydrosilasesquioxanes suggest a new way to study the pore-opening vibrations of zeolites. This approach simplifies the problem remarkably and thus leads to a better understanding of the more complex extended structures.

\section*{II. Experimental Section}

The normal mode calculations were performed by the Wilson GF matrix method\textsuperscript{28} using the computer program package QCMP067.\textsuperscript{29} The point charge model for describing molecular dipole moments was used to calculate relative infrared intensities. The atom charges, Si = +0.498, O = −0.305, and H = −0.040, were obtained from an extended-Hückel molecular orbital calculation\textsuperscript{30} of \( \text{H}_8\text{Si}_8\text{O}_{12} \) with the parameters reported in ref\textsuperscript{8b}. The bands of the calculated IR spectra were generated using a 1:1 mixture of a Lorentzian and a Gaussian curve which were adapted to the experimental bandwidths. The structure and the definition of the internal coordinates of the \((\text{HSi} \text{O}_3/2)_2\) \((n = 4, 5, 10, \text{ and } 12)\) are illustrated in Schemes 3S and 4S. For details we refer to ref\textsuperscript{14}. This definition of the internal coordinates is consistent with the usual conventions. It is applicable to all spherisoloxanes and results in 24 Si−H and

\section*{III. Correlation of the Vibrational Spectra of \( \text{H}_8\text{Si}_8\text{O}_{12} \) \ and \( \text{H}_{10}\text{Si}_{10}\text{O}_{15} \)}

\textbf{Structure and Irreducible Representations.} \( \text{H}_8\text{Si}_8\text{O}_{12} \) \( \text{and} \) \( \text{H}_{10}\text{Si}_{10}\text{O}_{15} \) single crystals show \( S_6 \) and \( C_2 \) molecular symmetry, respectively.\textsuperscript{2–4} The deviation from the “ideal” \( O_h \) and \( D_{5h} \) symmetry is small, and spectra measured in solution are fully compatible with \( O_h \) and \( D_{5h} \) symmetry, respectively. It is therefore convenient and useful to describe the vibrations of these molecules within the \( O_h \) and \( D_{5h} \) point groups, respectively, and to discuss deviations of this symmetry separately; see refs\textsuperscript{13–15}. On this basis the 78 vibrational degrees of freedom of \( \text{H}_8\text{Si}_8\text{O}_{12} \) and the 99 ones of \( \text{H}_{10}\text{Si}_{10}\text{O}_{15} \) are divided among the irreducible representations as follows (\( R \) = Raman active, \( IR \) = infrared active, \( in \) = inactive).

\( \text{O}_h\text{-}\text{H}_8\text{Si}_8\text{O}_{12} \):

\begin{equation}
\Gamma_{\text{vib}} = 3A_{1g}(R) + A_{2g}(in) + 4E_g(R) + 3T_{1u}(in) + 6T_{2g}(R) + 3A_{2u}(in) + 3E_u(in) + 6T_{1u}(IR) + 4T_{2u}(in) \quad (1)
\end{equation}

\( D_{5h}\text{-}\text{H}_{10}\text{Si}_{10}\text{O}_{15} \):

\begin{equation}
\Gamma_{\text{vib}} = 7A_{1'}(R) + 3A_{2'}(in) + 10E_{1'}(IR) + 11E_{2'}(R) + 3A_{1''}(in) + 6A_{2''}(IR) + 9E_{1''}(R) + 10E_{2''}(in) \quad (2)
\end{equation}

From this follows that the IR spectrum of \( \text{O}_h\text{-}\text{H}_8\text{Si}_8\text{O}_{12} \) consists of six and that of \( D_{5h}\text{-}\text{H}_{10}\text{Si}_{10}\text{O}_{15} \) of 16 fundamentals. The Raman spectrum of \( \text{O}_h\text{-}\text{H}_8\text{Si}_8\text{O}_{12} \) consists of 13 fundamentals, whereas 27 lines are expected for \( D_{5h}\text{-}\text{H}_{10}\text{Si}_{10}\text{O}_{15} \).

\textbf{\( \text{D}_{5h}\text{-}\text{D}_{5h} \) Correlation.} We consider the members of the oligomeric \((\text{HSi} \text{O}_3/2)_2\) molecules as a series of double-ring units with \( D_{5h} \) symmetry. This is illustrated in Figure 1. Since \( \text{D}_{5h} \) is a subgroup of the \( O_h \) point group, we apply a small distortion to the \( \text{O}_h\text{-}\text{H}_8\text{Si}_8\text{O}_{12} \) so that it fits into this series. The correlation

\begin{table}
\centering
\caption{Bond Lengths (Å) and Bond Angles (deg) Used for \( \text{H}_8\text{Si}_8\text{O}_{12} \) \, and \( \text{H}_{10}\text{Si}_{10}\text{O}_{15} \)}
\begin{tabular}{|l|c|c|}
\hline
\text{internal coordinate} & \( \text{H}_8\text{Si}_8\text{O}_{12} \) & \( \text{H}_{10}\text{Si}_{10}\text{O}_{15} \) \\
\hline
\text{R}(\text{Si−H}) & 1.48 & 1.48 \\
\text{r}(\text{Si−O}) & 1.62 & 1.61 \\
\text{s}(\text{Si−O}) & 1.60 & \\
\alpha(\text{O−Si−H}) & 109.5 & 109.5 \\
\beta(\text{O−Si−O}) & 109.5 & 109.5 \\
\gamma(\text{O−Si−H}) & 109.5 & 109.5 \\
\delta(\text{O−Si−O}) & 109.5 & 109.5 \\
\Phi(\text{Si−O−Si}) & 148.4 & 150.5 \\
\Psi(\text{Si−O−Si}) & 156.1 & \\
\hline
\end{tabular}
\end{table}
representations for all molecules. The \( E_{2g} \) and \( E_{2u} \) start to play others. Each row shows an equal number of irreducible representations. Each point group was obtained by considering the maximum common symmetry \( D_{nh} \). This result allows the assignment to a type of vibration based on the greatest contribution to the PED is somewhat arbitrary but still reasonable and useful.

In Figure 2 we compare the experimental IR spectra of \( H_8 Si_8 O_{12} \) (left) and \( D_8 Si_8 O_{12} \) (most right). We first observe that they bear a similar pattern and a similar intensity distribution. The similarity is easier to recognize in the calculated spectra because they contain no overtone and combination bands. The calculated spectra are in close agreement with the observed frequencies and the relative intensities. Harmonic correction of the experimental Si–H stretching frequencies shifts them close to the calculated values; see ref 14, Table 6. Symmetry lowering and correlation according to Table 2 leads to \( D_{6h} H_8 Si_8 O_{12} \) and from there to \( D_{3h} H_8 Si_8 O_{12} \), in which all IR and Raman active degenerate modes of \( O_6 H_8 Si_8 O_{12} \) appear as doublets and some of the inactive modes become IR or Raman active. Figure 2 illustrates that all experimentally observed fundamentals can be identified but that some are not resolved and a few are missing. The data in Table 3 show that missing lines have zero or very low intensity and that the splitting of nonresolved bands is smaller than the line widths of the corresponding absorptions. The assignment of the \( H_8 Si_8 O_{12} \) bands is based on the calculated frequencies and relative IR intensities. It was checked by evaluating the Teller–Redlich product rule and by comparing the result to the experimental spectrum of \( D_6 Si_8 O_{12} \). The calculated splitting of the two \( O_6 H_8 Si_8 O_{12} \) \( T_{1u} \) vibrations at 2381 and 1143 \( \text{cm}^{-1} \) to the \( D_{3h} H_8 Si_8 O_{12} \) \( E_1' \) plus \( A_2'' \) mode is too small to be observed under the applied conditions. The four \( T_{1u} \) lines at 881, 569, 481, and 397 \( \text{cm}^{-1} \) are split by 10, 40, 122, and 48 \( \text{cm}^{-1} \), respectively. However, at 569 and 481 \( \text{cm}^{-1} \) only one absorption was observed because of the low intensity of the \( A_2'' \) mode. Out of the four \( O_6 H_8 Si_8 O_{12} \) \( T_{2h} \) normal modes two components become IR active in the case of \( D_{3h} H_8 Si_8 O_{12} \). They show very weak intensity, in agreement with experiment.

The experimental Raman spectra of \( H_8 Si_8 O_{12} \) (left) and \( D_8 Si_8 O_{12} \) (right) in Figure 3 show a similar pattern and a
TABLE 3: IR and Raman Active Fundamentals (cm⁻¹) and Relative IR Intensities (in Parentheses) of H₆Si₆O₁₂ and H₁₀Si₁₀O₁₅

<table>
<thead>
<tr>
<th>symmetry</th>
<th>observed</th>
<th>calculated</th>
<th>potential energy distribution (%)</th>
<th>type of vibration</th>
<th>(\nu) (Si–H)</th>
<th>(\nu) (Si–O–Si)</th>
<th>(\delta) (O–Si–H)</th>
<th>(\delta) (Si–O–Si)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁g(R)</td>
<td>2302</td>
<td>2381</td>
<td>100 R</td>
<td>ν(Si–H)</td>
<td>2293</td>
<td>2381</td>
<td>100 R</td>
<td>ν(Si–H)</td>
</tr>
<tr>
<td>T₂g(R)</td>
<td>2291</td>
<td>2381</td>
<td>100 R</td>
<td>ν(Si–H)</td>
<td>2278</td>
<td>2381</td>
<td>100 R</td>
<td>ν(Si–H)</td>
</tr>
<tr>
<td>T₁d(IR)</td>
<td>2277 (11)</td>
<td>2381 (12)</td>
<td>100 R</td>
<td>ν(Si–H)</td>
<td>1147 (100)</td>
<td>1147 (100)</td>
<td>51 + 25 + 14 + 14 r</td>
<td>δ(O–Si–H)</td>
</tr>
<tr>
<td>T₁d(in)</td>
<td>1116</td>
<td>98 r</td>
<td>ν(Si–O–Si)</td>
<td>A₁g(in)</td>
<td>1176</td>
<td>97 s</td>
<td>65 s + 32 r</td>
<td>ν(Si–O–Si)</td>
</tr>
<tr>
<td>T₁d(IR)</td>
<td>1141 (100)</td>
<td>1143 (100)</td>
<td>97 r</td>
<td>ν(Si–O–Si)</td>
<td>1164 (100)</td>
<td>1164 (100)</td>
<td>97 r</td>
<td>ν(Si–O–Si)</td>
</tr>
<tr>
<td>T₁d(R)</td>
<td>1117</td>
<td>1116</td>
<td>97 r</td>
<td>ν(Si–O–Si)</td>
<td>1120 (100)</td>
<td>1120 (100)</td>
<td>63 r + 34 s</td>
<td>ν(Si–O–Si)</td>
</tr>
<tr>
<td>E₅(R)</td>
<td>932</td>
<td>922</td>
<td>77 α + 21 r</td>
<td>δ(O–Si–H)</td>
<td>1147</td>
<td>1147</td>
<td>51 + 25 + 14 + 14 r</td>
<td>δ(O–Si–H)</td>
</tr>
<tr>
<td>T₂d(in)</td>
<td>918</td>
<td>78 α + 20 r</td>
<td>δ(O–Si–H)</td>
<td>A₂u(in)</td>
<td>1120</td>
<td>1120</td>
<td>96 s</td>
<td>δ(O–Si–H)</td>
</tr>
<tr>
<td>E₅(R)</td>
<td>890</td>
<td>894</td>
<td>90 α + 10 r</td>
<td>ν(Si–O–Si)</td>
<td>1147</td>
<td>1147</td>
<td>63 r + 34 s</td>
<td>δ(O–Si–H)</td>
</tr>
<tr>
<td>T₆d(in)</td>
<td>881 (33)</td>
<td>881 (35)</td>
<td>95 α</td>
<td>ν(Si–O–Si)</td>
<td>1147</td>
<td>1147</td>
<td>63 r + 34 s</td>
<td>δ(O–Si–H)</td>
</tr>
<tr>
<td>T₁d(in)</td>
<td>865</td>
<td>99 α</td>
<td>δ(O–Si–H)</td>
<td>A₂g(in)</td>
<td>1120</td>
<td>1120</td>
<td>96 s</td>
<td>δ(O–Si–H)</td>
</tr>
<tr>
<td>E₅(R)</td>
<td>697</td>
<td>691</td>
<td>62 r + 23 α + 14 β</td>
<td>ν(Si–O–Si)</td>
<td>1147</td>
<td>1147</td>
<td>63 r + 34 s</td>
<td>δ(O–Si–H)</td>
</tr>
<tr>
<td>T₆d(in)</td>
<td>610</td>
<td>613</td>
<td>81 r + 10 α</td>
<td>ν(Si–O–Si)</td>
<td>1147</td>
<td>1147</td>
<td>63 r + 34 s</td>
<td>δ(O–Si–H)</td>
</tr>
<tr>
<td>A₁g(R)</td>
<td>580</td>
<td>576</td>
<td>53 + 36 α + 11 Φ</td>
<td>δ(O–Si–O)</td>
<td>1147</td>
<td>1147</td>
<td>63 r + 34 s</td>
<td>δ(O–Si–O)</td>
</tr>
<tr>
<td>T₆d(IR)</td>
<td>566 (1)</td>
<td>569 (0)</td>
<td>45 r + 39 β + 14 α</td>
<td>ν(Si–O–Si)</td>
<td>1147</td>
<td>1147</td>
<td>63 r + 34 s</td>
<td>δ(O–Si–O)</td>
</tr>
<tr>
<td>T₆d(IR)</td>
<td>465 (7)</td>
<td>481 (23)</td>
<td>53 r + 23 β + 17 α</td>
<td>ν(Si–O–Si)</td>
<td>1147</td>
<td>1147</td>
<td>63 r + 34 s</td>
<td>δ(O–Si–O)</td>
</tr>
<tr>
<td>A₁g(R)</td>
<td>456</td>
<td>446</td>
<td>99 r</td>
<td>ν(Si–O–Si)</td>
<td>1147</td>
<td>1147</td>
<td>63 r + 34 s</td>
<td>δ(O–Si–O)</td>
</tr>
<tr>
<td>E₅(R)</td>
<td>423</td>
<td>423</td>
<td>78 β + 19 r</td>
<td>δ(O–Si–O)</td>
<td>1147</td>
<td>1147</td>
<td>63 r + 34 s</td>
<td>δ(O–Si–O)</td>
</tr>
<tr>
<td>T₆d(R)</td>
<td>414</td>
<td>418</td>
<td>46 β + 29 α + 14 r + 11 Φ</td>
<td>δ(O–Si–O)</td>
<td>1147</td>
<td>1147</td>
<td>63 r + 34 s</td>
<td>δ(O–Si–O)</td>
</tr>
<tr>
<td>T₆d(IR)</td>
<td>399 (19)</td>
<td>397 (30)</td>
<td>79 β + 14 r</td>
<td>δ(O–Si–O)</td>
<td>1147</td>
<td>1147</td>
<td>63 r + 34 s</td>
<td>δ(O–Si–O)</td>
</tr>
<tr>
<td>T₆d(in)</td>
<td>356</td>
<td>89 β</td>
<td>δ(O–Si–O)</td>
<td>A₂g(in)</td>
<td>1147</td>
<td>1147</td>
<td>63 r + 34 s</td>
<td>δ(O–Si–O)</td>
</tr>
<tr>
<td>T₆d(in)</td>
<td>303</td>
<td>82 β + 12 r</td>
<td>δ(O–Si–O)</td>
<td>A₂g(in)</td>
<td>1147</td>
<td>1147</td>
<td>63 r + 34 s</td>
<td>δ(O–Si–O)</td>
</tr>
<tr>
<td>T₆d(R)</td>
<td>171</td>
<td>168</td>
<td>86 β</td>
<td>δ(O–Si–O)</td>
<td>1147</td>
<td>1147</td>
<td>63 r + 34 s</td>
<td>δ(O–Si–O)</td>
</tr>
<tr>
<td>E₅(R)</td>
<td>84</td>
<td>83</td>
<td>96 Φ</td>
<td>δ(Si–O–Si)</td>
<td>152</td>
<td>152</td>
<td>51 r + 18 β + 18 δ + 12 s</td>
<td>δ(Si–O–Si)</td>
</tr>
<tr>
<td>T₆d(in)</td>
<td>68</td>
<td>92 Φ</td>
<td>δ(Si–O–Si)</td>
<td>B₁g(in)</td>
<td>82</td>
<td>82</td>
<td>51 r + 18 β + 18 δ + 12 s</td>
<td>δ(Si–O–Si)</td>
</tr>
<tr>
<td>A₂g(in)</td>
<td>53</td>
<td>100 r</td>
<td>ν(Si–O–Si)</td>
<td>B₁g(in)</td>
<td>82</td>
<td>82</td>
<td>51 r + 18 β + 18 δ + 12 s</td>
<td>δ(Si–O–Si)</td>
</tr>
</tbody>
</table>
similar intensity distribution. The present program version does not allow one to calculate reliable Raman intensities. For this reason we restrict the discussion to the correlation diagram in the middle of Figure 3 and to the data collected in Table 3. We observe that the calculated frequencies agree well with the experimental values. The assignment of the lines of \( \text{H}_{10}\text{Si}_{10}\text{O}_{15} \) was checked by evaluating the Teller–Redlich product rule,\(^{38,39}\) based on the experimental \( \text{D}_{10}\text{Si}_{10}\text{O}_{15} \) spectrum.\(^{34}\) The calculated splitting of the six \( \text{T}_{2g} \) and the four \( \text{E}_{g} \) \( \text{O}_{h} \)-\( \text{H}_{8}\text{Si}_{8}\text{O}_{12} \) modes is small, in agreement with experiment. The lines at 423 and 168 cm\(^{-1}\) are exceptions and are split by 82 and 63 cm\(^{-1}\), respectively, in close agreement with experiment. The inactive \( \text{O}_{h} \)-\( \text{H}_{8}\text{Si}_{8}\text{O}_{12} \ \text{T}_{1g} \) and \( \text{A}_{2g} \) modes become Raman active for \( \text{D}_{5h} \)-\( \text{H}_{10}\text{Si}_{10}\text{O}_{15} \) but show very weak intensity.

**Discussion.** The small splitting of most of the degenerate modes, the weak intensity of the lines which become IR or Raman active in the case of \( \text{D}_{5h}\)-\( \text{H}_{10}\text{Si}_{10}\text{O}_{15} \), and the identical force field are the reasons for the close similarity of the
### Table 4: Group Frequencies (cm⁻¹) of Hydrosilasesquioxanes

<table>
<thead>
<tr>
<th>type of vibration</th>
<th>range of frequency</th>
<th>this work and ref 14</th>
<th>literature⁹</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν(Si–H)</td>
<td>&gt;2200</td>
<td>2260–2100 st</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>νₑ(Si–O–Si)</td>
<td>1200–1100</td>
<td>1130–1000 st</td>
<td>40, 41</td>
<td></td>
</tr>
<tr>
<td>δ(O–Si–H)</td>
<td>950–800</td>
<td>960–800 m</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>δ(Si–O–Si)</td>
<td>750–550</td>
<td>625–480 w</td>
<td>42, 44</td>
<td></td>
</tr>
<tr>
<td>δ(Si–O–Si)</td>
<td>500–150</td>
<td>580–250</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>δ(Si–O–Si)</td>
<td>&lt;100</td>
<td>120–50</td>
<td>45</td>
<td></td>
</tr>
</tbody>
</table>

a st = strong, m = medium, w = weak.

vibrational spectra of H₂₀Si₂₀O₃₀ and H₂₀Si₁₀O₁₅. H₂₀Si₂₀O₃₀ contains six 4-rings and H₁₀Si₁₀O₁₅ five 4- and two 5-rings; see Figure 1. Inspection of the PED analysis reported in Table 3 lays open the nature of the splitting of the degenerate IR and Raman active Oₖ(H₂₀Si₂₀O₃₀) modes upon symmetry reduction to D₄h and hence in the case of D₄h-H₂₀Si₁₀O₁₅. We observe that each of them splits into a vibration which may be associated with a 4- and 5-ring mode with the exceptions of the 418 and 397 cm⁻¹ lines, which split into two 4-ring normal modes.

The vibrations of H₂₀Si₂₀O₃₀ and H₁₀Si₁₀O₁₅ can be divided into the six distinct regions summarized in Table 4 and denoted as ν(Si–H), νₑ(Si–O–Si), δ(O–Si–H), νₐ(Si–O–Si), δ(O–Si–O), and δ(Si–O–Si). This means that the concept of group frequencies makes sense, although some normal modes do not fit into this general scheme. The frequency regions are in good agreement with those reported in the literature.⁴⁰–⁴⁵ The symmetric Si–H stretching frequencies are distinctly larger than those of HSi(SiMe₃)₃ and similar compounds.⁴⁶ We have shown that this difference is caused by the differences in the H–Si–O–Si conformation. The cage structure of the spheroidoloxanes dictates anti H–Si–O–Si conformation, whereas syn is the stable one for HSi(SiMe₃)₃.⁴⁷ The regions denoted by ν(Si–H), νₐ(Si–O–Si), and δ(Si–O–Si) contain normal modes, which may be considered as pure vibrations of the corresponding internal coordinates. However, some of the higher frequency δ(O–Si–H) modes do mix considerably with νₐ(Si–O–Si). In the lower νₐ(Si–O–Si) energy range we observe four vibrations which are primarily of δ(O–Si–O) character, namely, the bands at 576 cm⁻¹ (H₂₀Si₂₀O₃₀) and 613, 590, and 573 cm⁻¹ (H₁₀Si₁₀O₁₅). In the δ(O–Si–O) region five vibrations can be described as being of primarily νₐ(Si–O–Si) character, namely, the bands at 481 and 446 cm⁻¹ (H₂₀Si₂₀O₃₀) and 455, 450, and 334 cm⁻¹ (H₁₀Si₁₀O₁₅). The energy of these latter modes correlates with the size of the ring to which they belong. This will be the subject of section V.

### IV. Vibrational Spectra of H₂₀Si₂₀O₃₀ and H₂₄Si₂₄O₃₆

We now extend the discussion to the Iₙ-H₂₀Si₂₀O₃₀ and Oₙ-H₂₄Si₂₄O₃₆ molecules. These cages are parts of many silicates and zeolites¹³,²⁰,⁴⁸ and present models for many of these infinitely extended microporous materials.

**Structure and Irreducible Representations.** Since Iₙ-H₂₀Si₂₀O₃₀ and Oₙ-H₂₄Si₂₄O₃₆ have not been prepared so far, we apply bond lengths and bond angles based on the following reasoning. Tetrahedral angles at the silicon atoms are assumed. This leads to Si–O–Si angles of 177.¹⁴ and 160.⁵⁴ for H₂₀Si₂₀O₃₀ and H₂₄Si₂₄O₃₆, respectively. The corresponding Si–O bond lengths were calculated by means of the empirical relation \(d(\text{Si–O}) = 1.59 + [(180 – α)/2.1 \times 10^{-8}])\). This leads to 1.59 Å for all molecules. The Si–H bond lengths reported in Table 1 are used. The vibrational degrees of freedom for the Iₙ-H₂₀Si₂₀O₃₀ and the Oₙ-H₂₄Si₂₄O₃₆ are divided among the irreducible representations of the corresponding point groups as follows:

\[Iₙ-H₂₀Si₂₀O₃₀:\]
\[\Gamma_{\text{vib}} = 3Aₙ + 3T₁ₐ + 4T₂ₕ + 7Gₙ + 10Hₙ + 6Tₐₕ + 7Tₐ₂ + 7Gₙ + 7Hₙ \]

\[Oₙ-H₂₄Si₂₄O₃₆:\]
\[\Gamma_{\text{vib}} = 7A₁ₙ + 6A₂ₗ + 13Eₙ + 13T₁ₐ + 15T₂ₕ + 3A₄ₙ + 5A₂ₖ + 8Eₖ + 17T₁₉ + 16T₂₉ \]

From the selection rules follows that six T₁₉ → Aₖ transitions and 17 Tₐₖ → Aₖ transitions are IR active for H₂₀Si₂₀O₃₀ and H₂₄Si₂₄O₃₆, respectively. The three Aₖ → Aₖ and the 10 Hₙ → Aₖ transitions are Raman active in the case of H₂₀Si₂₀O₃₀, whereas seven A₁ₖ → Aₖ, 13 Eₙ → Aₖ, and 15 T₂ₕ → Aₖ transitions are Raman active for H₂₄Si₂₄O₃₆.

**Spectra and Normal Coordinate Analysis.** The calculated frequencies and the PED results are collected in Tables 5S and 6S, and the spectra are shown in Figures 4 and 5. The six IR active modes of H₂₀Si₂₀O₃₀ can be compared directly with the six IR active modes of H₂₀Si₂₀O₁₅. We observe in Figure 4 (left) that the three highest energy absorptions are almost equal in frequency and in relative intensity, while the 569, 481, and 397 cm⁻¹ Oₙ-H₂₀Si₂₀O₃₀ lines shift to 637, 284, and 439 cm⁻¹, respectively, and change in intensity. The PED analysis indicates that if a δ(O–Si–O) band increases in energy, its character is enhanced. The reverse is observed for νₐ(Si–O–Si) vibrations. The intensity changes of these lines correlate with the fact that symmetric Si–O–Si stretching vibrations show in general low infrared intensity, whereas δ(O–Si–O) movements give considerable IR absorptions.⁴³ On the right side of Figure 4 we compare the spectra of H₂₀Si₂₀O₁₅, H₂₀Si₁₀O₅₃, and H₂₄Si₂₄O₆. The spectra of the two latter ones are very similar. From the potential energy distribution analysis we find that each of the Oₙ-H₂₀Si₂₀O₁₅ IR lines at 1143, 881, 569, and 481 cm⁻¹ split into a 4- and 6-ring vibration in the case of the Oₙ-H₂₀Si₂₀O₆. The four Tₐ₂ₖ, Oₙ-H₂₀Si₂₀O₆ normal modes at 918, 682, 303, and 68 cm⁻¹ correlate with the T₁₉ 4-ring vibration at 894 cm⁻¹ and the T₁₉ 6-ring vibrations at 726, 309, and 85 cm⁻¹ of Oₙ-H₂₄Si₂₄O₆.

The Raman spectrum of H₂₀Si₂₀O₃₀ compares in a similar way to that of H₂₀Si₂₀O₁₅. Both show the same number of Raman active vibrations, three totally symmetric and 10 non-totally symmetric. The correlation of the energy levels is shown in Figure 5 (left). The broken lines connect modes of the same type. The ring-opening vibrations discussed in the next section are marked with the label RO. This correlation shows that for Iₙ-H₂₀Si₂₀O₃₀ out of the 13 Raman active lines of Oₙ-H₂₀Si₂₀O₁₅ only the three at 576, 446, and 418 cm⁻¹ shift considerably, namely, to 645, 251, and 336 cm⁻¹, respectively. This leads to very similar spectra for H₂₀Si₂₀O₃₀ and H₂₀Si₁₀O₁₅. The H₂₀Si₁₀O₁₅ via H₁₀Si₁₀O₁₅ to H₂₄Si₂₄O₆ correlation is more difficult due to the considerable increase of the number of Raman active modes from 13 to 27 to 35 lines, respectively. However, the number of totally symmetric normal modes remains constant from D₄h-H₂₀Si₂₀O₁₅ to D₄h-H₂₀Si₁₀O₁₅ to Oₙ-H₂₀Si₂₀O₆, and unambiguous correlation is possible. It is indicated by broken lines in Figure 5 (right) and shows that only the 423 cm⁻¹ line of H₂₀Si₁₀O₁₅ shifts considerably, namely, to 334 cm⁻¹ (D₄h-H₂₀Si₁₀O₁₅) and to 214 cm⁻¹ in the case of Oₙ-H₂₄Si₂₄O₆. This correlation corresponds to the transition of a 4- to a 5-ring and finally to a 6-ring vibration.
Discussion. \( \text{H}_8 \text{Si}_8 \text{O}_{12} \) and \( \text{H}_{20} \text{Si}_{20} \text{O}_{30} \) are composed of 4- and 5-rings, respectively. Both molecules have an equal number of IR and Raman active fundamentals. This enables us to correlate the normal modes associated with 4-rings with those associated with 5-rings in a direct way. The calculated spectra of \( \text{H}_8 \text{Si}_8 \text{O}_{12} \), \( \text{H}_{10} \text{Si}_{10} \text{O}_{15} \), and \( \text{H}_{24} \text{Si}_{24} \text{O}_{36} \) shown at the right side of Figures 4 and 5 give a clear qualitative picture of the development as the size and complexity of the molecules increase. In general, more bands appear in each region denoted in Table 4 when the molecules become larger, as expected. The infrared bands show in general an intensity enhancement in the \( \nu(Si-O-Si) \) and \( \delta(O-Si-O) \) regions. As in the previous section, we find that the concept of group frequencies is applicable and makes good sense for \( \text{H}_{20} \text{Si}_{20} \text{O}_{30} \) and \( \text{H}_{24} \text{Si}_{24} \text{O}_{36} \).

However, some vibrations do not fit into the general scheme of Table 4. We observe five \( \delta(O-Si-O) \) in the \( \nu(Si-O-Si) \) region, namely, at 645 and 637 cm\(^{-1} \) (\( \text{H}_8 \text{Si}_8 \text{O}_{12} \)), 620, 605, and 599 cm\(^{-1} \) (\( \text{H}_{10} \text{Si}_{10} \text{O}_{15} \)), while five \( \nu(Si-O-Si) \) appear in the \( \delta(O-Si-O) \) region, namely, at 336, 284, and 251 cm\(^{-1} \) (\( \text{H}_{24} \text{Si}_{24} \text{O}_{36} \)). The energy of the latter ones correlates with the size of the ring to which they belong, as will be shown in the next section.

V. Ring-Opening Vibrations of Spherosiloxanes

We define the ring-opening vibrations as normal modes in which all Si–O stretching and/or O–Si–O angle bending.
Defining the Ring-Opening Vibrations of $H_{8}Si_{8}O_{12}$

Scheme 5: Set of Equivalent Internal Coordinates

Displacements of the considered ring are in phase. To determine the symmetry species of these modes, we introduced new sets of internal coordinates as illustrated in Scheme 5 for the hexahedron which represents the $Si_8$ cage of $H_{8}Si_{8}O_{12}$. Each arrow is a representation of the corresponding 4-ring perpendicular to it. Therefore, the displacements of the new coordinates may be considered as a breathing motion of the ring. This leads to the following irreducible representations of these vibrations for the different cages.

Six 4-rings ($H_{8}Si_{8}O_{12}$):

$\Gamma_{RO}^{SR} = A_{1g} + E_{g} + T_{1u}$

Five 4- and two 5-rings ($H_{10}Si_{10}O_{15}$):

$\Gamma_{RO}^{SR} = A_{1} + E_{1} + E_{2}$

$\Gamma_{RO}^{SR} = A_{1} + A_{2}''$ (6)

12 5-rings ($H_{20}Si_{20}O_{30}$):

$\Gamma_{RO}^{SR} = A_{g} + H_{g} + T_{1u} + T_{2u}$

Six 4- and eight 6-rings ($H_{24}Si_{24}O_{36}$):

$\Gamma_{RO}^{SR} = A_{1g} + E_{g} + T_{1u}$

$\Gamma_{RO}^{SR} = A_{1g} + T_{2g} + A_{2u} + T_{1u}$

To apply this geometrical concept to the spheroloxiane cages, we must multiply each symmetry species with the number of appearances, which may be different from that of the polyhedron, because of the oxygen bridges. We have done this by visual representation of normal modes on a computer screen, using the computer program MOBY,$^{49}$ and analyzing all normal modes of the symmetry species in eq 6. The result of this analysis is given in eq 7.

$H_{8}Si_{8}O_{12}$: $\Gamma_{RO}^{SR} = A_{1g} + E_{g} + 2T_{1u}$

$H_{10}Si_{10}O_{15}$: $\Gamma_{RO}^{SR} = A_{1} + 2E_{1} + 2E_{2}$

$\Gamma_{RO}^{SR} = A_{1} + A_{2}''$ (7)

$H_{20}Si_{20}O_{30}$: $\Gamma_{RO}^{SR} = A_{g} + 2H_{g} + 2T_{1u} + 2T_{2u}$

$H_{24}Si_{24}O_{36}$: $\Gamma_{RO}^{SR} = A_{1g} + 2E_{g} + 2T_{1u}$

$\Gamma_{RO}^{SR} = A_{1g} + 2T_{2g} + A_{2u} + 2T_{1u}$

In Figure 6 the 11 IR active and in Figure 7 the 15 Raman active ring-opening normal modes of the investigated hydroxiloxianes are illustrated as projections. The three inactive ring-opening modes are not shown. Figures 6 and 7 are arranged such that the vibrational energy decreases from left to right. The filled circles correspond to the Si atoms, and the open circles, to oxygen atoms. We show the maximum potential energy geometries with amplitudes multiplied by a factor of 10. Because of the antisymmetric nature of the IR ring-opening vibrations in Figure 6, the top and the bottom ring openings are out of phase by 180°. The projection illustrates the maximum (solid lines) and the minimum (dashed lines) pore size. Since the top and the bottom Raman active pore opening vibrations are in phase, minimum and maximum positions are connected by solid lines.

Discussion. The energy regions of the 4-, 5-, and 6-ring-opening vibrations decrease from 490–390 to 440–250 to 340–210 cm$^{-1}$, respectively. The energy of the 5-ring- and 6-ring-opening vibrations depends on their character. The PED results in Tables 3, 5S, and 6S show that an increase in stretching character of a ring-opening mode correlates with a decrease in vibrational energy, but this is less pronounced in the case of the 4-ring modes. The totally symmetric vibrations show predominantly stretching character with the exception of the line at 451 cm$^{-1}$ for $H_{24}Si_{24}O_{36}$. They occur in specific regions, namely, at 460–440 cm$^{-1}$ for the 4-ring, at 340–250 cm$^{-1}$ for the 5-ring, and at 220–210 cm$^{-1}$ for the 6-ring.

In a previous study of the vibrations of zeolite A,$^{14}$ we discussed the four frequencies at 476, 288, 271, and 214 cm$^{-1}$, which are primarily of symmetric $T \rightarrow O \rightarrow T$ stretching character and fall into the $\delta(O \rightarrow T \rightarrow O)$ region. We assigned them to a D4R breathing mode, two 6-ring vibrations of the sodalite cage.
on the basis of a pseudolattice study of the D4R. Our analysis to the pore-opening vibration of the double 4-rings, respectively, Si\textsubscript{10}O\textsubscript{15}, at 336, 284, and 251 cm\textsuperscript{-1}, which they assigned to pore-opening vibrations. No and vibrations. This agrees well with the region of the four-ring-opening vibrations shows, however, that the reverse assignment might be correct. Dutta et al. reported two lines at 440 and 337 cm\textsuperscript{-1} of the ring-opening vibrations of zeolites. Flanigen et al. observed two lines at 285 and 214 cm\textsuperscript{-1} of the ring-opening vibrations of hydrosilasesquioxanes along the rotational axes perpendicular to the group frequencies in Table 4, namely, the modes at 481 and 446 cm\textsuperscript{-1} (H\textsubscript{8}Si\textsubscript{8}O\textsubscript{12}), at 455, 450, and 334 cm\textsuperscript{-1} (H\textsubscript{10}Si\textsubscript{10}O\textsubscript{15}), at 336, 284, and 251 cm\textsuperscript{-1} (H\textsubscript{20}Si\textsubscript{20}O\textsubscript{30}), and at 219 and 214 cm\textsuperscript{-1} (H\textsubscript{24}Si\textsubscript{24}O\textsubscript{36}). All of them can be identified as ring-opening vibrations.

We now compare the ring-opening modes of the investigated hydrosilasesquioxanes with the available literature data on pore-opening vibrations of zeolites. Flanigen et al. observed two bands at 378 and 260 cm\textsuperscript{-1} in the infrared spectrum of zeolite A, which they assigned to pore-opening vibrations. No and co-workers assigned them to normal modes of the 6-rings and to the pore-opening vibration of the double 4-rings, respectively, on the basis of a pseudolattice study of the D4R. Our analysis of the ring-opening vibrations shows, however, that the reverse assignment might be correct. Dutta et al. reported two lines at 410 and 337 cm\textsuperscript{-1} in the Raman spectrum of zeolite A, which are assigned to the motion of oxygen atoms of the double 4-rings. In a recent local-mode analysis of zeolite A two local modes at 446 and 431 cm\textsuperscript{-1} were attributed to the D4R breathing vibrations. This agrees well with the region of the four-membered ring-opening vibrations of hydrosilasesquioxanes. Bougeard and co-workers assigned the observed bands at 285 and 108 cm\textsuperscript{-1} to the pore opening of the double 4-rings and the breathing motion of the 8-ring (window), respectively, on the basis of a molecular dynamics study of window fluctuations in zeolite A. This can be compared to the decreasing frequency of the ring-opening vibration from ~440 (4-ring), to ~350 (5-ring), and to ~290 cm\textsuperscript{-1} (6-ring) we have observed. The 5-rings in the ZSM-5 framework cause a shift of the prominent Raman band from ~490 to ~390 cm\textsuperscript{-1}. This compares well to our observation that the 446 cm\textsuperscript{-1} double 4-ring breathing mode of H\textsubscript{5}Si\textsubscript{5}O\textsubscript{12} shifts to 334 cm\textsuperscript{-1} in H\textsubscript{10}Si\textsubscript{10}O\textsubscript{15}.

Acknowledgment. This work is financed by the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung (Project NF 20-040598.94/1) and by the Schweizerisches Bundesamt für Energiewirtschaft (Project BEW (93)-034). We would like to thank Claudia Marcolli for her contributions and Dr. Roman Imhof and Dr. Martin Bärtsch for measuring the infrared and the FT-Raman spectra.

Supporting Information Available: Structures and internal coordinates of H\textsubscript{8}Si\textsubscript{8}O\textsubscript{12}, H\textsubscript{10}Si\textsubscript{10}O\textsubscript{15}, H\textsubscript{20}Si\textsubscript{20}O\textsubscript{30}, and H\textsubscript{24}Si\textsubscript{24}O\textsubscript{36} (Schemes 3S and 4S) and calculated IR and Raman active vibrations (Schemes 3S and 4S).

References and Notes


