

# Review

## Monosubstituted Octasilasesquioxanes\*

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Octasilasesquioxanes are cube-shaped molecules consisting of a  $\text{Si}_8\text{O}_{12}$  core and eight reactive sites, which can, in principle, all be functionalized differently. This review article provides an overview of the work, which is concerned with the monosubstituted species,  $\text{R}'\text{R}_7\text{Si}_8\text{O}_{12}$ , where  $\text{R}'$  and  $\text{R}$  are two different substituents, such as organic or organometallic groups or single atoms (H, Cl). Three synthetic routes have been used so far to prepare monosubstituted silasesquioxanes: co-hydrolysis of trifunctional organo- or hydro-silanes, substitution reactions with retention of the siloxane cage, and corner-capping reactions. These three different strategies are discussed in this review. Various spectroscopic techniques that have been applied to characterize these molecules — X-ray diffraction, NMR, IR and Raman spectroscopy as well as mass spectrometry — are treated. A main focus is the notion of ring-opening vibration, which is supposed to be generally applicable to microporous materials, especially zeolites. A simple model for explaining the nature of ring-opening vibrations is presented. Based on the new possibilities offered by functionalized silasesquioxanes, challenging perspectives for the synthesis of novel materials are discussed. Copyright © 1999 John Wiley & Sons, Ltd.

**Keywords:** octasilasesquioxanes; synthesis; structure ring-opening vibrations

## INTRODUCTION

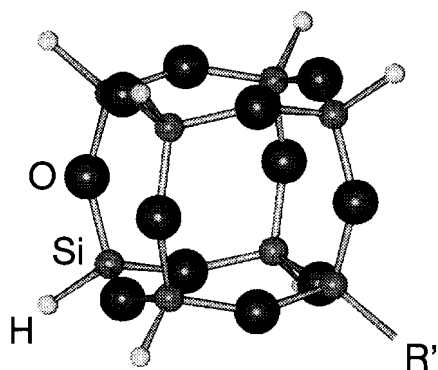
Polyhedral oligomeric silasesquioxanes  $(\text{RSiO}_{1.5})_{2n}$  ( $n = 2, 3, 4$ ) have attracted considerable interest in the last few years. They are accessible by hydrolysis of trifunctional  $\text{RSiY}_3$  molecules<sup>1–4</sup> and can be modified by a number of substitution reactions. Thus, functionalized silasesquioxanes have become available, which are interesting as precursors to organolithic macromolecular materials<sup>5–7</sup> or hybrid inorganic–organic materials.<sup>8–12</sup> Apart from the silasesquioxanes with silicon–oxygen frameworks, different hetero- and metalla-siloxanes<sup>13</sup> have been prepared, such as alumino-, titana-, and gallium-silasesquioxanes where one<sup>14–20</sup> or several<sup>21–27</sup> silicon atoms are replaced. Silasesquioxanes have been successfully viewed as model compounds for zeolites and silica surfaces<sup>28–33</sup> and some of them have been thoroughly investigated by different spectroscopic techniques, i.e. X-ray or neutron diffraction<sup>34–39</sup> and vibrational<sup>29,30,40</sup> and NMR spectroscopies.<sup>41,42</sup> Although most work has concentrated on the cube-shaped octasilasesquioxanes, several species with six to 18 silicon atoms have been synthesized and characterized as well.<sup>3,30,43–47</sup> The octasilasesquioxanes offer eight reactive sites, one at each vertex, which can, in principle, all be functionalized differently. Most work has so far concentrated on the homofunctionalized species, yet a more specific derivatization with diverse sets of functional groups would provide still greater variety. Thus multifunctional cubes could be obtained, which can be more exactly tailored to a particular use.

This review article will concentrate on the substitution at one vertex, which can be regarded as the initial step to heterogeneously functionalized silasesquioxanes. A general review on octasilasesquioxanes has appeared recently.<sup>48</sup> Monosubstitution leads to  $\text{R}'\text{R}_7\text{Si}_8\text{O}_{12}$  molecules as shown in Fig. 1 for  $\text{R} = \text{H}$ . Several studies have appeared in the last few years which were concerned with the synthesis and characterization of such monosubstituted silasesquioxanes. It is the purpose of this

\* Dedicated to Professor Peter Jutzi on the occasion of his 60th birthday.

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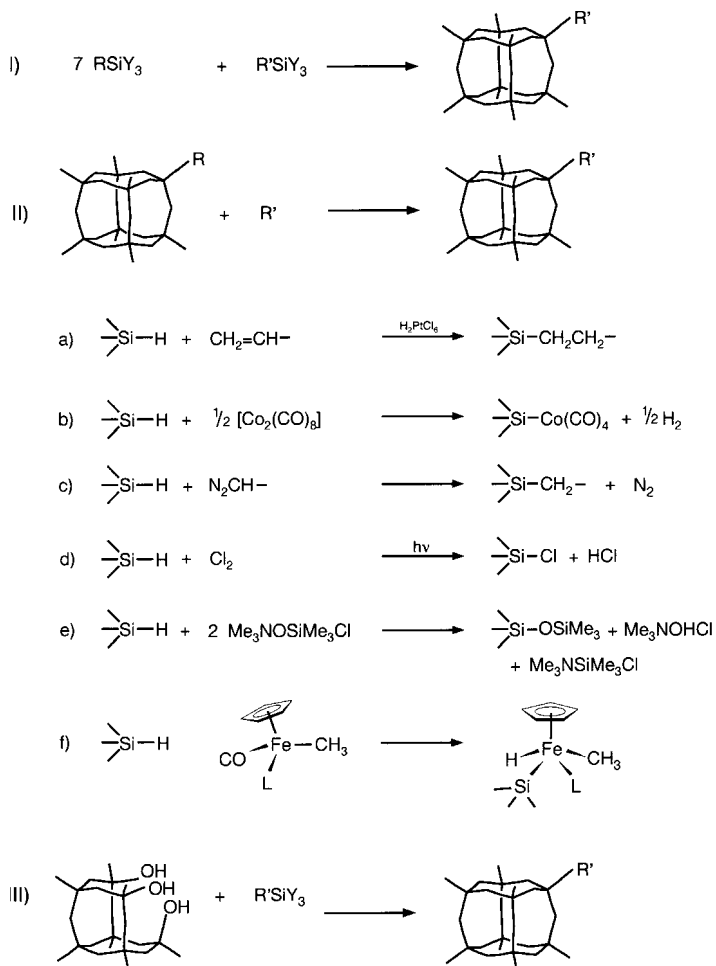


**Figure 1** The octasilasesquioxane cage  $R'R_7Si_8O_{12}$  for  $R = H$ .

review to give an overview of this work. Based on these new possibilities, challenging perspectives are discussed and a simple model for explaining the nature of ring-opening vibrations is presented.

## SYNTHESIS

Three general ways of synthesizing monosubstituted silasesquioxanes  $R'R_7Si_8O_{12}$  have been used so far. They are summarized in Scheme 1. The polycondensation of monomers, route I, represents the classical method of synthesizing silasesquioxanes. When this reaction is carried out in the presence of monomers with different R groups, a mixture of heterosubstituted compounds is ob-



**Scheme 1** Three general ways (I–III) of synthesizing monosubstituted octasilasesquioxanes.

**Table 1. Monosubstituted octasilasesquioxanes, R'R<sub>7</sub>Si<sub>8</sub>O<sub>12</sub>, reported in the literature<sup>a</sup>**

R	R'	Route <sup>a</sup>	References
H	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub> , CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	II	49
H	[(η-C <sub>5</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> )Fe(η-C <sub>5</sub> H <sub>5</sub> )]	II	50
H	Co(CO) <sub>4</sub>	II	51
H	CHCHC <sub>6</sub> H <sub>5</sub>	II	52
H	CH <sub>2</sub> CH <sub>2</sub> C <sub>10</sub> H <sub>7</sub> , CH <sub>2</sub> CH <sub>2</sub> C <sub>14</sub> H <sub>9</sub> , O(H <sub>7</sub> Si <sub>8</sub> O <sub>12</sub> )	II	53
H	C <sub>6</sub> H <sub>5</sub>	I	54
H	(CH <sub>2</sub> ) <sub>3</sub> (OCH <sub>2</sub> CH <sub>2</sub> ) <sub>18</sub> OCH <sub>3</sub> , (CH <sub>2</sub> ) <sub>3</sub> (OCH <sub>2</sub> CH <sub>2</sub> ) <sub>40</sub> OCH <sub>3</sub>	II	56
CH <sub>3</sub> , CHCH <sub>2</sub>	CHCH <sub>2</sub> , CH <sub>3</sub>	I	55
C <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> [Cr(CO) <sub>3</sub> ]	II	53
C <sub>2</sub> H <sub>5</sub>	CHCH <sub>2</sub>	I	56 <sup>b</sup>
C <sub>2</sub> H <sub>5</sub>	(CH <sub>2</sub> ) <sub>8</sub> CHCH <sub>2</sub> , (CH <sub>2</sub> ) <sub>8</sub> CHBrCH <sub>2</sub> Br	II	57
C <sub>3</sub> H <sub>7</sub>	3-ClC <sub>3</sub> H <sub>6</sub> , 3-IC <sub>3</sub> H <sub>6</sub> , 3-HSC <sub>3</sub> H <sub>6</sub> , C <sub>3</sub> H <sub>5</sub>	I	56 <sup>b</sup>
c-C <sub>6</sub> H <sub>11</sub>	[O(AlSi <sub>7</sub> O <sub>12</sub> )(c-C <sub>6</sub> H <sub>11</sub> ) <sub>7</sub> ] <sup>-</sup> [Me <sub>4</sub> Sb] <sup>+</sup>	III	16
c-C <sub>6</sub> H <sub>11</sub>	H, Cl, D	III	16, 58
c-C <sub>6</sub> H <sub>11</sub>	CHP(CH <sub>3</sub> ) <sub>3</sub> , CHP(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	III	58
c-C <sub>6</sub> H <sub>11</sub>	CHCHC <sub>6</sub> H <sub>5</sub> , CHCHC(CH <sub>3</sub> )CH <sub>2</sub> , CHCH(CH <sub>2</sub> ) <sub>8</sub> CHCH <sub>2</sub> , <i>p</i> -CHCHC <sub>6</sub> H <sub>4</sub> OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> , <i>p</i> -CHCHC <sub>6</sub> H <sub>4</sub> OC(O)C(CH <sub>3</sub> )CH <sub>2</sub> , <i>p</i> -CHCHC <sub>6</sub> H <sub>4</sub> Br	III	58
c-C <sub>6</sub> H <sub>11</sub>	H, CHCH <sub>2</sub> , CH <sub>2</sub> CHCH <sub>2</sub> , (CH <sub>2</sub> ) <sub>6</sub> CHCH <sub>2</sub> , CHCH(CH <sub>2</sub> ) <sub>8</sub> CHCH <sub>2</sub>	III	16, 59
c-C <sub>6</sub> H <sub>11</sub> , c-C <sub>5</sub> H <sub>9</sub>	(CH <sub>2</sub> ) <sub>3</sub> OC(O)C(CH <sub>3</sub> )CH <sub>2</sub>	III	60
c-C <sub>6</sub> H <sub>11</sub> , c-C <sub>5</sub> H <sub>9</sub>	<i>p</i> -(CH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHCH <sub>2</sub>	III	61
(CH <sub>2</sub> ) <sub>3</sub> (OCH <sub>2</sub> CH <sub>2</sub> ) <sub>4</sub> OH	(CH <sub>2</sub> ) <sub>2</sub> (Si(CH <sub>3</sub> ) <sub>2</sub> O) <sub>3</sub> Si(CH <sub>3</sub> ) <sub>2</sub> Bu	II	62
OSi(CH <sub>3</sub> ) <sub>2</sub> H	OSi(CH <sub>3</sub> ) <sub>2</sub> [CH <sub>2</sub> CH <sub>2</sub> (η-C <sub>5</sub> H <sub>4</sub> )Fe(η-C <sub>5</sub> H <sub>5</sub> )]	II	66
OSiCH <sub>3</sub>	CH <sub>3</sub>	I	64

<sup>a</sup> Initial step of monosubstitution according to Scheme 1.

<sup>b</sup> F. Dietsche, R. Harselmann, H. Frey and R. Mülhaupt, unpublished results.

tained, including monosubstituted ones. Route II is probably the most generally applicable. In Scheme 2 a selection of substitution reactions is shown with octahydrosilasesquioxane as starting material (IIa–f). Reaction types IIa–c have been applied successfully to prepare monosubstituted silasesquioxanes. Reactions II d and II e have been used to replace all substituents; by adjusting the ratio of the reactants, it should also be possible to obtain a considerable yield of the monosubstituted products. Reaction II f has not yet been applied to silasesquioxanes and it would be interesting to know if this reaction proceeds without destroying the siloxane cage. Route III was developed by Feher *et al.* It leads selectively to the monosubstituted compound as the only product. Its application range is, however, still limited because the incompletely condensed silasesquioxane is only available with large organic groups as substituents. Table 1 gives a selection of the monosubstituted silasesquioxanes that have been synthesized so far.

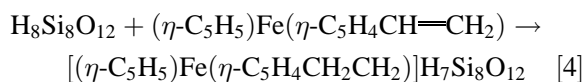
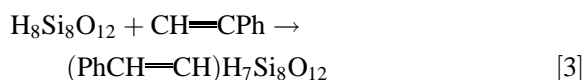
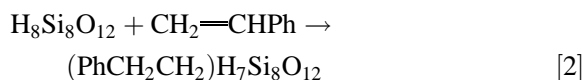
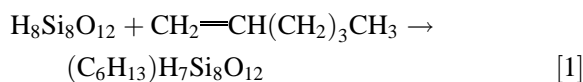
### Route I: co-hydrolysis of trifunctional organo- or hydro-silanes

The first monosubstituted octasilasesquioxanes were prepared by co-hydrolysis of RSiY<sub>3</sub> and R'SiY<sub>3</sub> monomers, where R and R' are hydrogen atoms or organic groups.<sup>1</sup> This synthesis gives a mixture of products with all possible ratios of R/R'. The dependence on the reaction conditions has been investigated by Martynova and Chupakhina for the co-hydrolysis of CH<sub>3</sub>SiCl<sub>3</sub>/C<sub>2</sub>H<sub>5</sub>SiCl<sub>3</sub> and CH<sub>3</sub>Si(OCOCH<sub>3</sub>)<sub>3</sub>/C<sub>2</sub>H<sub>5</sub>Si(OCOCH<sub>3</sub>)<sub>3</sub>.<sup>55</sup> Maximum amounts of monosubstituted species are realized by co-hydrolysis of the monomers RSiY<sub>3</sub> and R'SiY<sub>3</sub> in a ratio of 1:7. However, the absolute and relative yields depend strongly on the reaction time and the functional group Y. To obtain pure substances subsequent separation of the mixtures is indispensable.

In our group co-hydrolysis of  $\text{HSiCl}_3$  and  $\text{PhSiCl}_3$  was applied to synthesize  $\text{PhH}_7\text{Si}_8\text{O}_{12}$ .<sup>54</sup> Similarly,  $\text{MeSi}_8\text{O}_{19}(\text{SiMe}_3)_7$  and the cubic octameric anion  $\text{MeSi}_8\text{O}_{19}^{7-}$  are formed by exchange of  $\text{Si}(\text{O}^-)_4$  units in the silicate species  $\text{Si}_8\text{O}_{20}^{8-}$ .<sup>63,64</sup>

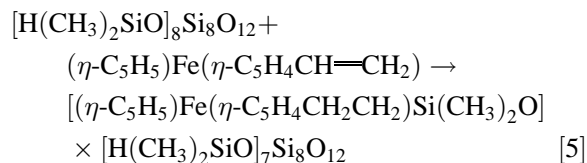
## Route II: substitution reactions with retention of the siloxane cage

Reaction type IIa — platinum-catalysed hydrosilylation<sup>65</sup> — represents an important and well-established way to form Si–C bonds in organo-silicon chemistry. It takes place under mild conditions and leaves the siloxane cage intact. Its attraction stems from the fact that it is generally applicable because the starting material,  $\text{H}_8\text{Si}_8\text{O}_{12}$ , is easily accessible by the synthetic procedure introduced by Agaskar.<sup>3</sup> The hydrosilylation reactions 1–4



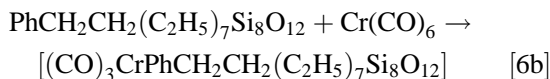
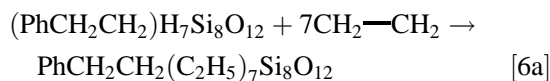
(catalyst:  $\text{H}_2\text{PtCl}_6$ ) leading to monosubstituted products have been reported by us:<sup>49,50,52</sup>

Whereas reactions 1–3 yielded organic monosubstituted silicon–oxygen cages, reaction 4 led to the first organometallic monosubstituted octanuclear silasesquioxane. A very similar reaction was carried out by Morán *et al.*,<sup>66</sup> starting from  $[\text{H}(\text{CH}_3)_2\text{SiO}]_8\text{Si}_8\text{O}_{12}$  and using Karstedt's catalyst:



A reaction scheme involving two hydrosilylations was successfully applied to obtain another

monosubstituted organometallic compound: starting from the product of reaction 2, the molecule  $[(\text{CO})_3\text{CrPhCH}_2\text{CH}_2(\text{C}_2\text{H}_5)_7\text{Si}_8\text{O}_{12}]$  was prepared in two steps:<sup>53</sup>



Several groups reported hydrosilylations leading to eightfold or mixed substituted octasilasesquioxanes. Thus, starting from  $\text{H}_8\text{Si}_8\text{O}_{12}$  or  $[\text{H}(\text{CH}_3)_2\text{SiO}]_8\text{Si}_8\text{O}_{12}$  highly functionalized silasesquioxanes were obtained<sup>9,10,57,62,67–76</sup> (see also F. Dietsche, R. Hanselmann, H. Frey and R. Mülhaupt, unpublished results) Although the addition at the terminating carbon atom ( $\beta$ -position) is the dominating one,  $\alpha$  and  $\beta$  additions usually occur. The mode of addition is influenced by substituent effects, catalyst effects and/or process conditions. A mixture of mono- and higher-substituted products is usually formed, which can be subsequently separated by HPLC.<sup>56,77,78</sup>

Reaction type IIb leads to a monosubstituted hydrosilasesquioxane with a silicon–cobalt bond.<sup>51</sup> It was applied by Harrison and Kannengiesser to synthesize the twofold-substituted  $[(\text{Co}(\text{CO})_4)_2\text{H}_6\text{Si}_8\text{O}_{12}]$ .<sup>8</sup> Jutzi recently succeeded in preparing the fully substituted molecule  $[(\text{Co}(\text{CO})_4)_8\text{Si}_8\text{O}_{12}]$ .<sup>‡</sup>

Reaction type IIc provides an elegant method of synthesizing monosubstituted products by the insertion of carbenes into the Si–H bond of silicon–oxygen cages as shown in Scheme 1. In this reaction a diazoacetate is irradiated in the presence of the cage compound (Maitland Jones Jr, private communication, 1996).

A number of reactions have so far been reported only for the substitution of *all* functional groups, e.g. photochemical chlorination leading to  $\text{Cl}_8\text{Si}_8\text{O}_{12}$  (IId),<sup>79</sup> Palladium-catalysed deuterium exchange of  $\text{H}_8\text{Si}_8\text{O}_{12}$ ,<sup>40,80</sup> and silylation of  $[\text{Si}_8\text{O}_{20}]^{8-}$  leading to siloxane-substituted cages  $(\text{RSiO})_8\text{Si}_8\text{O}_{12}$ .<sup>6,81,82</sup> Siloxane-substituted products have also been obtained by reaction of the hydrosilasesquioxane  $\text{H}_8\text{Si}_8\text{O}_{12}$  with main-group ethers or  $\text{Me}_3\text{NOSiR}_3\text{Cl}$ ,<sup>17,43,83</sup> as shown in Scheme 1, Reaction IIe. Once the siloxane cage is functionalized it can be further modified.<sup>7,84–86</sup> In principle, these reactions should also be applicable to synthesis of the monosubstituted species. Reaction IIc represents a challenging possibility, which

‡ M. Rattay, D. Fenske and P. Jutzi, *Organometallics* **17**, 2930 (1998).

has not yet been tried, to connect an iron atom directly to the silasesquioxane unit. It is also possible that methane is released in this reaction. Based on the reactions which have been successful so far, and based on theoretical reasoning,<sup>87</sup> it seems probable that substitution reactions with retention of the siloxane cage generally proceed via a radical-type five-coordinated silicon intermediate.

### Route III: corner-capping reactions

This type of reaction represents a method of synthesizing monosubstituted octasilasesquioxanes as the only products. It was developed by Feher and co-workers and starts from the incompletely condensed  $R_7Si_7O_9(OH)_3$  molecule.<sup>14,16,17,88</sup> The three silanol groups represent a very reactive site, which can be converted with  $RSiCl_3$  to give the fully condensed product. Variation of the R group on the silane enables a variety of monofunctionalized siloxane cages to be synthesized.<sup>89,90</sup> Subsequent transformations can be carried out until the desired functionality is obtained. In this respect, the compounds  $[(c-C_6H_{11})_7Si_8O_{12}(CHPR_3)]$  (R = Me or Ph) are worth mentioning. They react with a variety of aldehydes as Wittig reagents and are synthesized starting from  $(c-C_6H_{11})_7Si_8O_{12}Cl$  or

$(c-C_6H_{11})_7Si_8O_{12}H$  in a reaction with  $Me_3PCH_2$  and  $Ph_3PCH_2$ , respectively.<sup>58</sup> Interestingly, the analogous reactions of  $H_8Si_8O_{12}$  or  $Cl_8Si_8O_{12}$  with phosphoranes do not lead to the desired products.

Moreover, incompletely condensed silasesquioxanes offer a source for the generation of hetero- and metalla-siloxanes, where a hetero main-group or a transition-metal element is introduced into the silicon-oxygen framework.<sup>13-17,91,92</sup>

The drawback of the corner-capping reaction is the long reaction time needed for the synthesis of the starting material,  $R_7Si_7O_9(OH)_3$ . Although synthetically useful quantities of cyclohexylsilane-triol can be obtained in one or two weeks by filtering at early reaction times, this synthesis, which was first reported by Brown and Vogt,<sup>93</sup> takes more than a year to give good yields. Moreover this reaction is at present still restricted to a very small number of R groups, namely R =  $c-C_5H_9$ ,  $c-C_6H_{11}$  and  $c-C_7H_{13}$ .

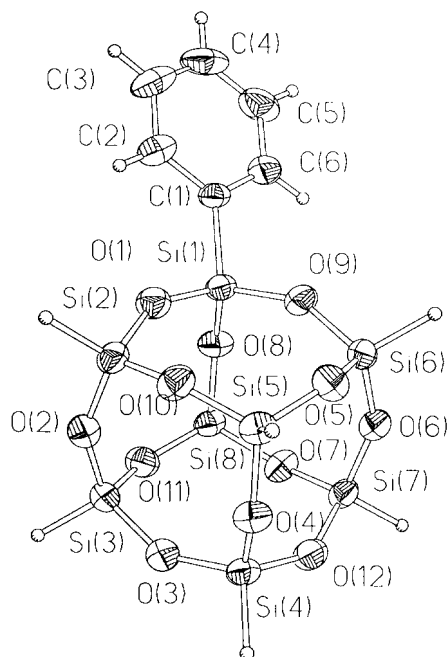
## CHARACTERIZATION

### X-ray diffraction

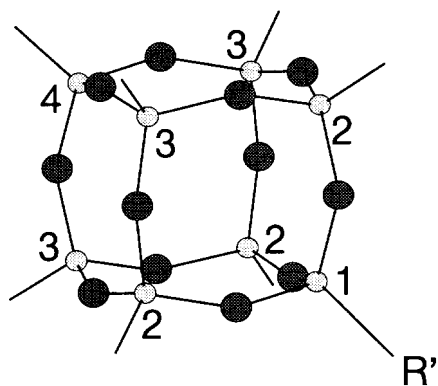
The X-ray diffraction structures of three monosubstituted octahydrosilasesquioxanes,  $(C_6H_{13})_7H_7Si_8O_{12}$ ,  $PhH_7Si_8O_{12}$  and  $[Co(CO)_4(H_7Si_8O_{12})]$ , have been reported so far.<sup>51,54,94</sup> That of  $PhH_7Si_8O_{12}$  is shown in Fig. 2. These molecules show overall  $C_1$  symmetry, whereas the siloxane cages maintain approximate  $C_3$  symmetry.

Two factors influence the molecular geometry of the monosubstituted cage compounds: intermolecular interactions in the crystalline state and deformation features on the silicon tetrahedron attached to the substituent. The intermolecular interactions, which are due to relatively short  $Si \cdots O$  contacts, are most pronounced in  $H_8Si_8O_{12}$ ,<sup>35,36</sup> where they are responsible for the symmetry reduction from ideal  $O_h$  to an effective molecular  $T_h$  symmetry in the crystal.  $H_8Si_8O_{12}$  exhibits eight  $Si \cdots O$  contacts shorter than 3.7 Å. There are four for  $[Co(CO)_4(H_7Si_8O_{12})]$  and two for  $(C_6H_{13})_7H_7Si_8O_{12}$ .  $PhH_7Si_8O_{12}$  shows no such short  $Si \cdots O$  contacts. The number of short  $Si \cdots O$  contacts is proportional to the magnitude of the out-of-plane deformation of the O atoms and to an increase of the crystal density.

The deformation on the silicon tetrahedron attached to the substituent is induced by the substituent group, which cause the silicon atom



**Figure 2** Crystal structure of  $PhH_7Si_8O_{12}$  with atomic labeling and anisotropic displacement parameters at the 30% probability level.



**Figure 3** The four sets of equivalent silicon atoms in monosubstituted silasesquioxanes.

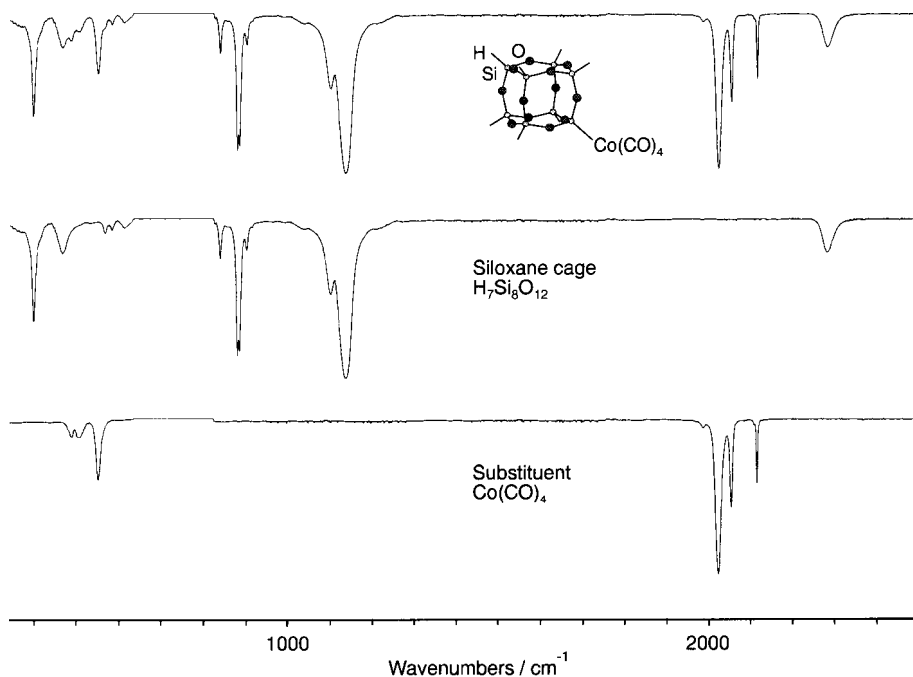
that binds to the substituent to move out of the cage. Thus the body diagonal Si...Si is elongated. This effect is largest for  $[\text{Co}(\text{CO})_4(\text{H}_7\text{Si}_8\text{O}_{12})]$ .<sup>51</sup>

The Si–O distances of the monosubstituted substances range between 1.588 and 1.622 Å. The mean values, 1.606(8) Å for  $(\text{C}_6\text{H}_{13})\text{H}_7\text{Si}_8\text{O}_{12}$ , 1.612(5) Å for  $\text{PhH}_7\text{Si}_8\text{O}_{12}$  and 1.612(3) Å for  $[\text{Co}(\text{CO})_4(\text{H}_7\text{Si}_8\text{O}_{12})]$ , are slightly smaller than that for  $\text{H}_8\text{Si}_8\text{O}_{12}$  [1.618(1) Å]. It was found that the O–Si–O angles  $\alpha$  are inversely proportional to the Si–O distances  $d$ , and that the relationship conforms

to the equation  $d(\text{Si}-\text{O})/\text{\AA} = 1.59 + [1.6 \times 10^{-8}(180 - \alpha)^4]$ .<sup>94</sup> The Si–O–Si angles vary from 144 to 153°. This range is even larger for heterosilasesquioxanes of the type  $[(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}\text{M}]$ . For  $\text{M}=\text{P}$  the Si–O–Si angles vary from 136 to 162°.<sup>91</sup>

## NMR

$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectroscopies are frequently used to identify and characterize silasesquioxanes. Hendan and Marsmann<sup>56</sup> studied the  $^{29}\text{Si}$  NMR spectra of the monosubstituted substances  $\text{R}'\text{R}_7\text{Si}_8\text{O}_{12}$ , for  $\text{R}=\text{n-C}_3\text{H}_7$ ,  $\text{R}'=3\text{-ClC}_3\text{H}_6$ ,  $3\text{-IC}_3\text{H}_6$ ,  $3\text{-HSC}_3\text{H}_6$  and  $\text{C}_3\text{H}_5$  as well as  $\text{R}=\text{C}_2\text{H}_5$ ,  $\text{R}'=\text{C}_2\text{H}_3$ . Assuming  $\text{C}_{3v}$  symmetry, four singlets in a 1:3:3:1 ratio are expected for the four sets of equivalent silicon atoms (Fig. 3). This pattern was only observed for  $\text{R}=\text{n-C}_3\text{H}_7$  and  $\text{R}'=3\text{-IC}_3\text{H}_6$ . In the other substances investigated the two peaks of the silicon atoms with no adjacent  $\text{R}'$ -substituted silicon atom fall together and only three peaks could be distinguished. The  $^{29}\text{Si}$  NMR spectra of the inorganic or metallorganic substituted  $[\text{Co}(\text{CO})_4(\text{H}_7\text{Si}_8\text{O}_{12})]$  and  $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)(\text{H}_7\text{Si}_8\text{O}_{12})]$  showed the expected four signals with relative intensities 1:3:3:1.<sup>51,53</sup> The connectivity of the silicon atoms can be



**Figure 4** Transmission IR spectrum of  $[\text{Co}(\text{CO})_4(\text{H}_7\text{Si}_8\text{O}_{12})]$  divided into the lines due to the siloxane cage and the substituent.

monitored by  $^{29}\text{Si}$  2D-INADEQUATE NMR spectroscopy.<sup>56,95</sup>

## IR and Raman spectroscopy

We have measured IR and Raman spectra of different monosubstituted octasilasesquioxanes. The four molecules  $\text{RH}_7\text{Si}_8\text{O}_{12}$  [R = Ph, PhCH=CH, PhCH<sub>2</sub>CH<sub>2</sub> and Co(CO)<sub>4</sub>] have been investigated in detail on the basis of a normal coordinate analysis.<sup>52,54,96</sup> We observed that the spectra can be treated as a superposition of the peaks of the substituent, the siloxane cage and the vibrations involving the Si-C bond, as shown in Figs 4 and 5 for R = Co(CO)<sub>4</sub>.

### Siloxane cage vibrations

In Tables 2 and 3 the IR and Raman peaks due to the siloxane cage are listed. Compared with  $\text{H}_8\text{Si}_8\text{O}_{12}$  no large frequency shifts are observed. It can be seen that the introduction of a substituent gives rise to additional peaks and peak splittings. Most spectral features of the siloxane cages could

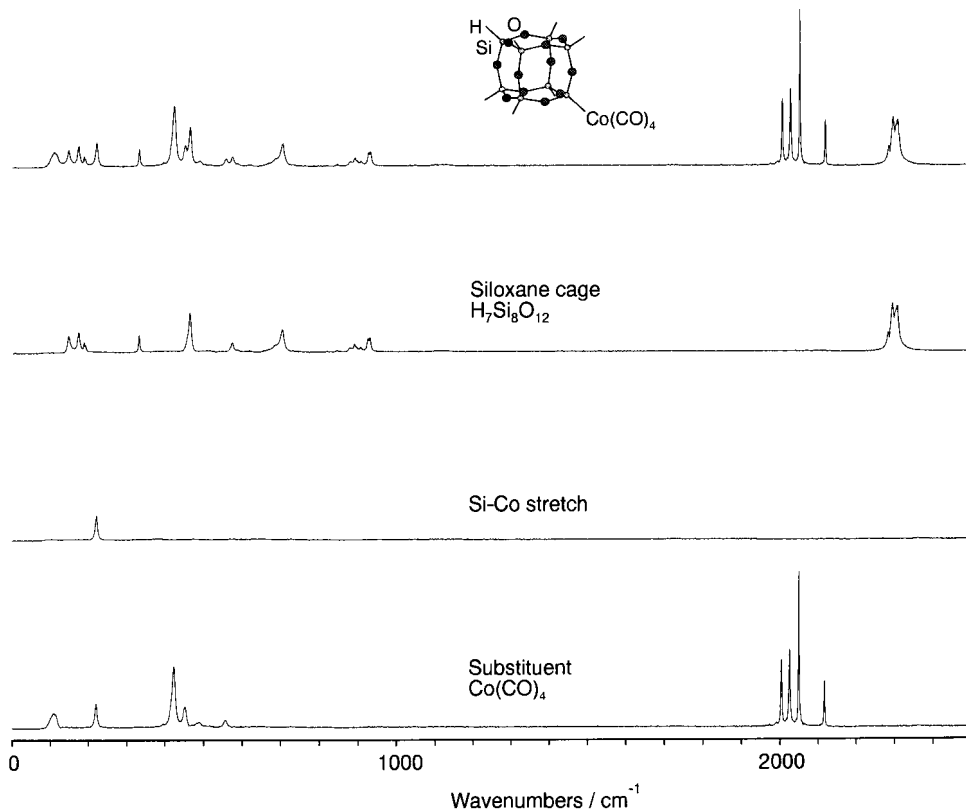
be understood by assuming a local  $C_{3v}$  symmetry; vibrations indicating a lower symmetry occurred in all monosubstituted compounds and were due to vibrational coupling with modes of the substituent.

### Si-X stretching vibrations

The molecules  $\text{PhH}_7\text{Si}_8\text{O}_{12}$ ,  $(\text{PhCH}=\text{CH})\text{H}_7\text{Si}_8\text{O}_{12}$  and  $(\text{PhCH}_2\text{CH}_2)\text{H}_7\text{Si}_8\text{O}_{12}$  allow the investigation of the organic-substituted siloxane cage  $\text{CH}_7\text{Si}_8\text{O}_{12}$ , each contributing a case of an Si-C<sub>phenyl</sub>, Si-C<sub>vinyl</sub> and Si-C<sub>alkyl</sub> bond, respectively. The Si-C stretching frequencies, force constants and bond orders of the different types of Si-C bonds are listed in Table 4. It can be seen that the bond orders correlate well with the stretching force constants. On this basis a stretching force constant for the Si-C<sub>acetyl</sub> bond was extrapolated.

The Si-Co stretching vibration of  $[\text{Co}(\text{CO})_4(\text{H}_7\text{Si}_8\text{O}_{12})]$  was assigned to a peak of medium intensity at  $220\text{ cm}^{-1}$ , which exhibits 33% Si-Co stretching character in the potential energy distribution.

The Si-X stretching frequencies of the cage-



**Figure 5** Fourier-transform Raman spectrum of  $[\text{Co}(\text{CO})_4(\text{H}_7\text{Si}_8\text{O}_{12})]$  divided into the lines due to the siloxane cage, the substituent and the Si-Co stretch.

**Table 2. IR frequencies of the siloxane cage vibrations of various monosubstituted octahydrosilasesquioxanes,  $\text{RH}_7\text{Si}_8\text{O}_{12}$ , and the unsubstituted compound (R = H)**

Wavenumber ( $\text{cm}^{-1}$ )						Symmetry		Vibration type
R = $\text{Co}(\text{CO})_4$	R = Ph	R = CH=CHPh	R = $\text{CH}_2\text{CH}_2\text{Ph}$	R = $\text{C}_6\text{H}_{13}$	R = H	$C_{3v}$	$O_h$	
2276, 2276	2274, 2274	2275, 2275	2274, 2274	2274	2277	$A_1, E$	$T_{1u}$	$\nu(\text{Si-H})$
1138, 1138	1140, 1140	1140, 1140	1141, 1141	1139	1141	$A_1, E$	$T_{1u}$	$\nu_{\text{asym}}(\text{Si-O-Si})$
1101						$A_1, E$	$T_{2g}$	$\nu_{\text{asym}}(\text{Si-O-Si})$
916	915	915	916	916		$E$	$E_g$	$\delta(\text{O-Si-H})$
—, 904	—, 905	—, 905	—, 905	—, 905		$A_2, E$	$T_{2u}$	$\delta(\text{O-Si-H})$
—, 886	—, 886	—, 886	—, 886	—, 887		$A_1, E$	$T_{2g}$	$\delta(\text{O-Si-H})$
886, 881	886, 881	886, 883	886, 882	887, 882	881	$A_1, E$	$T_{1u}$	$\delta(\text{O-Si-H})$
857, 840	—, 844	854, 848	852, 846	—, 846		$A_2, E$	$T_{1g}$	$\delta(\text{O-Si-H})$
	718/704					$E$	$E_g$	$\nu_{\text{sym}}(\text{Si-O-Si})$
613			607, 622/18			$A_1, E$	$T_{2g}$	$\nu_{\text{sym}}(\text{Si-O-Si})$
			573	572		$A_1$	$A_{1g}$	$\delta(\text{O-Si-O})$
584, 565	—, 568		—, 568		566	$A_1, E$	$T_{1u}$	$\nu_{\text{sym}}(\text{O-Si-O})$
469, 469	475, 475	469, 469	468, 468	468	465	$A_1, E$	$T_{1u}$	$\nu_{\text{sym}}(\text{O-Si-O})$
399, 399	401, 401	402, 388	395, 402	401	399	$A_1, E$	$T_{1u}$	$\delta(\text{O-Si-O})$

**Table 3. Raman frequencies of the siloxane cage vibrations of various monosubstituted octahydrosilasesquioxanes  $\text{RH}_7\text{Si}_8\text{O}_{12}$  and the unsubstituted compound (R = H)**

Wavenumber ( $\text{cm}^{-1}$ )					Symmetry		Vibration type
R = $\text{Co}(\text{CO})_4$	R = Ph	R = CH=CHPh	R = $\text{CH}_2\text{CH}_2\text{Ph}$	R = H	$C_{3v}$	$O_h$	
2297	2291	2295	2295	2302	$A_1, E$	$A_{1g}$	$\nu(\text{Si-H})$
2285, 2301/292	2278, 2285	2284, 2278	2286, 2286	2296, 2286	$A_1, E$	$T_{2g}$	$\nu(\text{Si-H})$
2285, 2274	2269, 2275				$A_1, E$	$T_{1u}$	$\nu(\text{Si-H})$
~1117, ~1117	1140, 1121	1119, 1119	1118, 1118	1117	$A_1, E$	$T_{2g}$	$\nu_{\text{asym}}(\text{Si-O-Si})$
928/923	925	927	928/26	932	$E$	$E_g$	$\delta(\text{O-Si-H})$
—, 904	—, 904	—, 900	—, 899		$A_2, E$	$T_{2u}$	$\delta(\text{O-Si-H})$
893, 888	893, 889	894, 890	890, 888	897, 883	$A_1, E$	$T_{2g}$	$\delta(\text{O-Si-H})$
878, 875	875, 868	874, 874	873, 871		$A_1, E$	$T_{1u}$	$\delta(\text{O-Si-H})$
—, 841	—, 839	847, 842	—, 840		$A_2, E$	$T_{1g}$	$\delta(\text{O-Si-H})$
701	712/707	706	726/703	697	$E$	$E_g$	$\nu_{\text{sym}}(\text{Si-O-Si})$
684	682, 682	688, 684/682	685		$A_2, E$	$T_{2u}$	$\nu_{\text{sym}}(\text{Si-O-Si})$
~616		597, —		610	$A_1, E$	$T_{2g}$	$\nu_{\text{sym}}(\text{Si-O-Si})$
571	580	575	575	580	$A_1$	$A_{1g}$	$\delta(\text{O-Si-O})$
585, —	—, 569	532, 572			$A_1, E$	$T_{1u}$	$\nu_{\text{sym}}(\text{O-Si-O})$
461 (449)	462	455	452	456	$A_1$	$A_{1g}$	$\nu_{\text{sym}}(\text{O-Si-O})$
	427	423/427	410, 423	414	$A_1, E$	$T_{2g}$	$\delta(\text{O-Si-O})$
	412	411	410	423	$E$	$E_g$	$\delta(\text{O-Si-O})$
	392		405, 389		$A_1, E$	$T_{1u}$	$\delta(\text{O-Si-O})$
			—, 340	352	$A_2, E$	$T_{1g}$	$\delta(\text{O-Si-O})$
329	333	315	314		$A_1$	$A_{2u}$	$\delta(\text{O-Si-O})$
147, 173	143, 172/169	187, 171	173, 173	171	$A_1, E$	$T_{2g}$	$\delta(\text{O-Si-O})$
190/187	165/157	156/140	142		$E$	$E_u$	$\delta(\text{O-Si-O})$
	112/97	92		84	$E$	$E_g$	$\delta(\text{Si-O-Si})$

shaped silasesquioxanes were found to be higher than those of comparable siloxane compounds without cage structure (Table 5). Molecular orbital calculations on  $\text{XSi}(\text{OSiMe}_3)_3$  (X = H,  $\text{CH}_3$ , Cl) in its *syn* and *anti* positions (Fig. 6) showed that the

Si-X bond orders depend on the conformation.<sup>97</sup> Figure 7 shows that the Si-H bond order (*B*) is highest for the *anti* conformation ( $\varphi = 0$ ) and decreases with increasing dihedral angle  $\varphi$ . Since the cage structure of  $\text{X}_8\text{Si}_8\text{O}_{12}$  requires the *anti*



**Table 4.** Si–C stretching frequencies, bond distances and force constants for various monosubstituted octasilasesquioxanes

Bond type	IR (cm <sup>-1</sup> )	Raman (cm <sup>-1</sup> )	Calcd (cm <sup>-1</sup> )	Contribution of Si–C coordinate (%)	$F(v_{\text{SiC}})$ (mdyn Å <sup>-1</sup> )	Si–C bond order	Substituent
Si–C <sub>alkyl</sub>	785 790	784	782	39%	3.03	0.638	PhCH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>13</sub>
Si–C <sub>vinyl</sub>	821	821	817	49%	3.36	0.659	PhCH=CH
Si–C <sub>phenyl</sub>	730	730	731	30%	3.39	0.664	Ph
Si–C <sub>acetyl</sub>					3.67 <sup>a</sup>	0.682	PhC≡C

<sup>a</sup> Extrapolated.**Table 5.** Experimental FT-Raman Si–X stretching frequencies (cm<sup>-1</sup>)

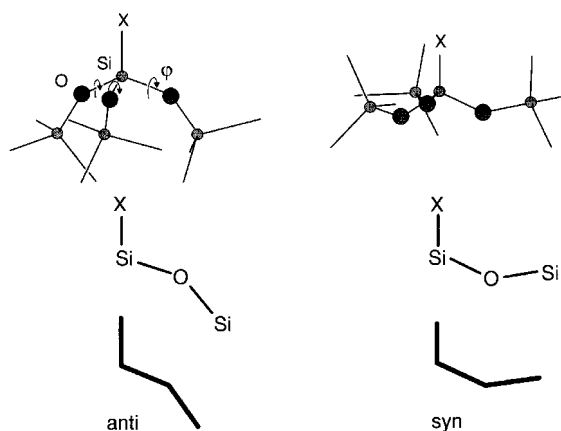
Molecule	X = H	X = CH <sub>3</sub>	X = Cl
X <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> <sup>a</sup>	2302	819	733
XSi(OSiMe <sub>3</sub> ) <sub>3</sub>	2207	748 <sup>d</sup>	588
XSi(OSiMe <sub>2</sub> H) <sub>3</sub>	2223 <sup>b</sup> /2214 <sup>c</sup>		
X <sub>10</sub> Si <sub>10</sub> O <sub>15</sub> <sup>a</sup>	2293		

<sup>a</sup> Totally symmetric stretching vibration.<sup>b</sup> Reference 110.<sup>c</sup> Reference 111.<sup>d</sup> Assignment according to Reference 111.

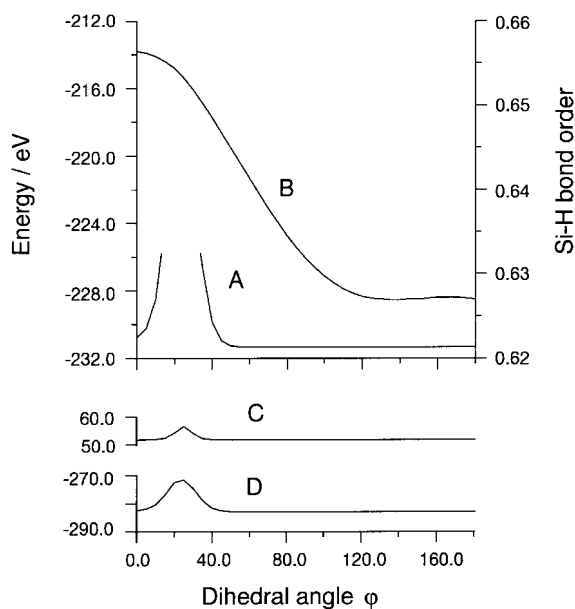
conformation and *syn* is the stable one in XSi(OSiMe<sub>3</sub>)<sub>3</sub>, the Si–X bond order for X<sub>8</sub>Si<sub>8</sub>O<sub>12</sub> is higher than for XSi(OSiMe<sub>3</sub>)<sub>3</sub>.

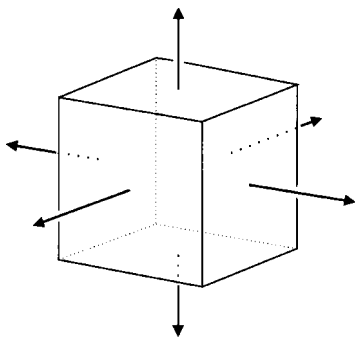
### Ring-opening vibrations

An interesting feature found in the spectra of silasesquioxanes are the ring-opening vibrations. They are defined as 'normal modes in which all

**Figure 6** *Anti* ( $\varphi = 0^\circ$ ) and *syn* ( $\varphi = 180^\circ$ ) conformations of XSi(OSiMe<sub>3</sub>)<sub>3</sub>.

*Si–O stretching and/or O–Si–O angle bending displacements of the considered ring are in phase*.<sup>30</sup> The ring-opening vibrations of the hydrosilasesquioxanes suggest a new way to study the pore-opening vibrations of zeolites and should facilitate the understanding of these more complex extended structures. For a cube, six ring-opening modes are expected, one for each ring, as shown in Fig. 8. Assuming an ideal  $O_h$  symmetry, they belong to the irreducible representations  $A_{1g}$ ,  $E_g$  and  $T_{1u}$ . To apply this geometrical concept to H<sub>8</sub>Si<sub>8</sub>O<sub>12</sub>

**Figure 7** Energies and bond order of HSi(OSiMe<sub>3</sub>)<sub>3</sub> as a function of the dihedral angle  $\varphi$  (A): total energy  $E_{\text{tot}}$ ; (B) Si–H bond order; (C) core–core repulsion  $E_{\text{rep}}$ ; (D) extended-Hückel binding energy ( $\Delta E_{\text{EHMO}}$ ). The barrier in the total energy (A) at about  $30^\circ$  is enormous and caused by orbital interactions (D) and core–core repulsion (C).



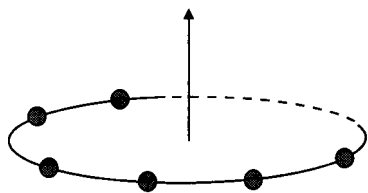
**Figure 8** Set of equivalent internal coordinates defining the ring-opening vibrations of an octasilasesquioxane.

the displacements of the oxygen atoms must be considered, which leads to an  $A_{1g}$  and  $E_g$  but two  $T_{1u}$  ring-opening vibrations. Ring-opening modes were also found in the monosubstituted compounds and appear in the same frequency regions. We draw attention to the intense peak in the Raman spectrum of  $H_8Si_8O_{12}$  at  $456\text{ cm}^{-1}$ , which is due to a ring-opening vibration and which shows a specific dependence on the different substituents.<sup>96</sup>

When we consider only one ring consisting of  $N$  atoms and  $N$  bond stretching coordinates  $\Delta r$ , as shown on the left-hand side of Fig. 9, the totally symmetric stretching coordinate  $\Delta R$  of a ring can be expressed as Eqn 7:

$$\Delta R = \frac{1}{N^{1/2}} (\Delta r_1 + \Delta r_2 + \dots + \Delta r_N) \quad [7]$$

Such ring-opening coordinates are supposed to give strong signals in the Raman spectra. If the atoms are assumed to be equally spaced, the frequency of the ring-opening vibration can be calculated as a function of the number of atoms,  $N$ ,



where  $N \geq 3$ . To do this, the  $G$  element  $g$  of the coordinate  $\Delta R$  has to be evaluated first. As each atom performs an equivalent movement and contributes an equal amount to the  $G$  element, it is sufficient to look in detail at the movement of only one atom. The right-hand side of Fig. 9 shows that the resulting coordinate for each atom describes a radial movement, which amounts to:

$$b = \frac{1}{N^{1/2}} 2 \sin\left(\frac{\alpha}{2}\right) = \frac{1}{N^{1/2}} 2 \sin\left(\frac{\pi}{N}\right) \quad [8]$$

where the net displacement  $b$  is a dimensionless quantity. The  $G$  element  $g$  is given as the sum of the contributions of the atoms on the ring:

$$g = \frac{N}{m} b^2 = \frac{4}{m} \sin^2\left(\frac{2\pi}{N}\right)$$

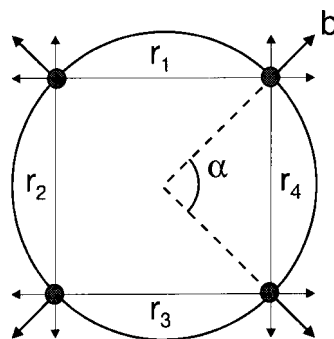
and the frequency  $\nu$  equals:

$$\nu = \frac{1}{2\pi} \sqrt{f \cdot g} = \frac{1}{\pi} \sqrt{\frac{f}{m}} \sin\left(\frac{\pi}{N}\right) \quad [9]$$

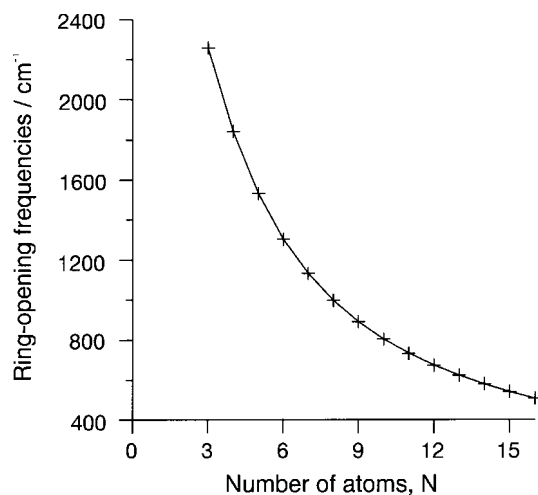
where  $m$  is the mass of an atom and  $f$  the bond stretching force constant. Equation [9] shows that for constant  $f$  and constant  $m$ , the frequency of the ring-opening vibration depends only on the number of atoms on the ring. It seems not to depend on the radius of the ring,  $a$ . Yet, since a constant  $f$  implies a constant bond length  $r$ , increasing the number of atoms and keeping  $f$  constant leads to an increasing radius  $a$  of the ring:

$$a = \frac{r}{2 \sin(\pi/N)} \quad [10]$$

Thus, the frequency  $\nu$  can also be expressed as a



**Figure 9** Idealized ring-opening coordinates for the general case of  $N$  atoms equally spaced on a ring (left-hand side), and for the four-membered-ring (right-hand side).



**Figure 10** Totally symmetric ring-opening frequencies for rings of different sizes:  $N = 3-16$ ;  $f = 1 \text{ mdyn } \text{Å}^{-1}$ ;  $m = 1 \text{ u}$ .

function of the radius  $a$ :

$$\nu = \frac{1}{\pi} \sqrt{\frac{f}{m}} \cdot \frac{r}{2a} \quad [11]$$

The dependence of the ring-opening frequencies on  $N$  is shown in Fig. 10 for  $f = 1 \text{ mdyn } \text{Å}^{-1}$  and  $m = 1 \text{ u}$  ( $\text{u}$  is the atomic mass unit). It shows that the ring-opening frequencies decrease with increasing ring size.

In order to estimate values for the ring-opening vibrations of hydrosilasesquioxanes, this simple model can be extended to rings consisting of atoms with two different masses, where the atoms are equally spaced and arranged alternately. When the angle bending coordinates are neglected, the coordinate  $R$  is still a normal coordinate of the system and  $g$  is then given as:

$$g = \left( \frac{N}{m_1} + \frac{N}{m_2} \right) b^2 \quad [12]$$

where  $m_1$  and  $m_2$  are the two different masses and  $N$  the number of atoms with mass  $m_1$ . Table 6 shows the values obtained for the four, five- and six-rings of cyclic siloxanes (where the numbers refer to four, five and six silicon atoms, respectively). This calculation was performed with the Si–O stretching force constant determined for  $\text{H}_8\text{Si}_8\text{O}_{12}$  and the atomic masses of oxygen and silicon. The values obtained are close to the upper frequency limit of the ring-opening vibrations, which were determined by a normal coordinate analysis of the molecules  $O_h\text{-H}_8\text{Si}_8\text{O}_{12}$ ,  $D_{5h}\text{-H}_{10}\text{Si}_{10}\text{O}_{15}$ ,  $I_h\text{-H}_{20}\text{Si}_{20}\text{O}_{30}$  and  $O_h\text{-H}_{24}\text{Si}_{24}\text{O}_{36}$ .<sup>30</sup> The simple model of equally

**Table 6.** Ring-opening frequencies of siloxane rings ( $\text{cm}^{-1}$ )

Ring size	Hydrosilasesquioxanes <sup>a</sup>	Siloxane rings <sup>b</sup>
4	390–490	499
5	250–440	403
6	219–340	337

<sup>a</sup> Reference 30.

<sup>b</sup> Calculated with  $f = 5.1 \text{ mdyn } \text{Å}^{-1}$ ,  $m_1 = 16 \text{ u}$ ,  $m_2 = 28 \text{ u}$ .

spaced atoms on a ring leads to a correct estimate of the ring-opening frequencies and makes it easy to understand this special vibration, which has an important analogy in pore-opening vibrations of microporous materials.<sup>29,30</sup>

## Mass spectrometry

The mass spectra of different octasilasesquioxanes have been studied in detail by Aebi *et al.*<sup>53,78</sup> This analysis included the monosubstituted compounds  $\text{R}'\text{R}_7\text{Si}_8\text{O}_{12}$  ( $\text{R}' = \text{CH}_2\text{CH}_2\text{Ph}$ ,  $\text{CH}(\text{CH}_3)\text{Ph}$ ,  $\text{C}(\text{CH}_2)\text{Ph}$ ,  $\text{CH}=\text{CHPh}$  and  $\text{R} = \text{H}$  as well as  $\text{R}' = \text{C}(\text{CH}_2)\text{Ph}$ ,  $\text{CH}=\text{CHPh}$  and  $\text{R} = \text{Et}$ ). It showed that the fragmentation pattern is dependent on the nature of the substituents. The  $\text{Si}_8\text{O}_{12}$  framework is more easily cracked for the monosubstituted compounds with  $\text{R} = \text{H}$ , than for those with  $\text{R} = \text{Et}$ . This is in agreement with the result obtained for the uniformly substituted octasilasesquioxanes, where  $\text{H}_8\text{Si}_8\text{O}_{12}$  shows stronger degradation of the inner structure than  $\text{Me}_8\text{Si}_8\text{O}_{12}$  and  $\text{Et}_8\text{Si}_8\text{O}_{12}$ . The monosubstituted compounds investigated expose a strong signal for the molecular ion, most probably due to the aromatic rings, which hold the positive charge and thus stabilize the molecular ion. Doubly charged ions could also be found.

## DISCUSSION

Polyhedral oligomeric silasesquioxanes have been investigated by several groups as polymerizable reagents in the synthesis of hybrid materials with desirable physical properties such as thermoplasticity and elasticity. The discrete structure of the silasesquioxane components in such materials enables the establishment of property relationships based on chain structure and composition. This is in contrast to the situation for polysilasesquioxanes, for which the absolute polymeric structures are largely unknown. Monofunctionalized octasila-

sesquioxanes are used as organic–inorganic hybrid monomers. Homopolymerization and copolymerization with an organic monomer leads to ‘pendant’ and ‘triblock’ architectures, respectively.<sup>89</sup>

Polymers with such structures were synthesized by Lichtenhan *et al.* A corner-capping reaction of  $R_7Si_7O_9(OH)_3$  ( $R = c-C_6H_{11}$  or  $c-C_5H_9$ ) yielded the monomer with a styryl- or vinyl-functionalized alkyl chain as a polymerizable group. The incorporation of an octasilasesquioxane effects an increase of the glass transition temperature,  $T_g$ , above that of resins without silasesquioxane side groups.<sup>59–61,98–103</sup>

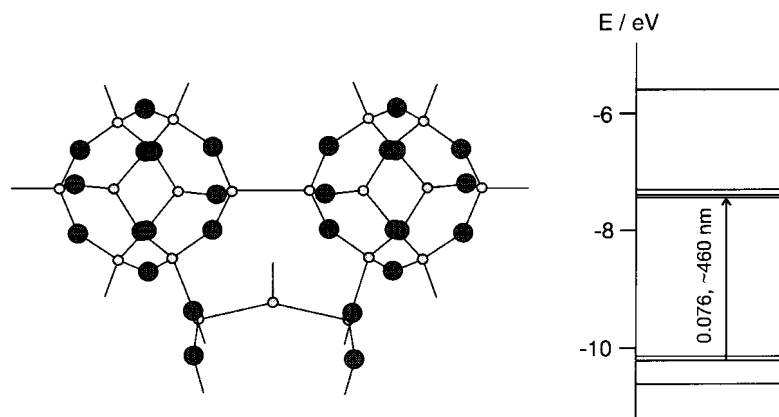
Frey *et al.* reported the synthesis of ethene and propene copolymers containing octasilasesquioxane side groups. Comonomer incorporation of up to 25 wt% was achieved and accounted for an improved thermostability with respect to polyethene. In this reaction a monovinyl-functional octasilasesquioxane, which was synthesized by hydrosilylation starting from  $H_8Si_8O_{12}$ , was used as comonomer.<sup>57</sup> This synthetic procedure allows a larger variability of the seven inert alkyl groups surrounding the siloxane cage compared with corner-capping reactions. Based on a monosubstituted octasilasesquioxane with a hydrophilic substituent they also succeeded in preparing a novel type of amphiphile (F. Dietsche, R. Harselmann, H. Frey and R. Mülhaupt, unpublished results).

Laine *et al.* have shown that functionalized octasilasesquioxanes with different numbers of methacrylate or epoxy groups form thermally and photocurable monomers, which are interesting as precursors in processing composites, especially curable dental composites.<sup>9,10,70,71,104,105</sup>

Synthetic methods of performing substitution reactions at only one vertex of the siloxane cage are a requirement for functionalizing the silasesquioxane with different substituents in a step-by-step procedure. The control of the individual reaction steps would allow the synthesis of donor–acceptor systems of the type  $R'R''R_6Si_8O_{12}$ , where the donor and acceptor groups could be separated by  $-Si(OSi)_nOSi-$  bridges of different lengths:  $n = 0, 1, 2$ . Such systems could be compared with their purely organic analogues, based on  $c-C_6H_{11}$  bridges for example.<sup>48</sup>

In the last few years, considerable attention was dedicated to the investigation of luminescent silicon compounds.<sup>106,107</sup> To estimate the potential of silasesquioxanes as building blocks for luminescent model substances, a quantum-chemical investigation on the EHMO-EDiT level was carried out in our group.<sup>108,109</sup> It showed that the energy gap is reduced from 11.2 eV in  $H_8Si_8O_{12}$  to 10.13 eV in  $(H_7Si_8O_{12})_2$  and 6.65 eV in  $(H_7Si_8O_{12})_2H_6Si_8O_{12}$ . The last value will not change notably when the chain is extended to infinity. The energy gap is reduced, however, when the number of cross-links between the cages is augmented as shown in Fig. 11. The compound  $(H_6Si_8O_{12})_2(Si(OH)_2)_2SiH_2$  exhibits an energy gap of *ca* 2.7 eV (*ca* 460 nm). Since the oscillator strength is considerable, significant luminescence can be expected, thus showing a route to luminescent molecular silicon compounds.

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**Figure 11** Structure and energy levels of  $(H_6Si_8O_{12})_2(Si(OH)_2)_2SiH_2$ . This substance exhibits an oscillator strength of 0.076 for the strongest transition at *ca* 460 nm.

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