Normal coordinate analysis of $H_8Si_8O_{12}$

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Abstract—Normal coordinate analysis of the fundamental vibrations of $H_8Si_8O_{12}$ has been carried out. Because of the octahedral symmetry, the 78 vibrational degrees of freedom lead to 33 different vibrations, six of which are infrared active, 13 are Raman active and 14 are inactive. From the internal coordinates one gets 116 symmetry coordinates. We describe a straightforward method for determining the internal symmetry coordinates of any molecular system. Internal coordinates, symmetry force constants, the full set of orthonormal symmetry coordinates as well as the 38 redundant orthonormal symmetry coordinates of $H_8Si_8O_{12}$ are tabulated. The potential energy distribution analysis shows that most of the fundamental vibrations can be very well interpreted in terms of the internal vibrations $\nu(Si-H)$, $\nu(Si-O)$, $\delta(Si-H)$, $\delta(O-Si-O)$ and $\delta(Si-O-Si)$ which makes it easy to compare them with vibrations observed in other silsesquioxanes and similar silicon compounds.

INTRODUCTION

The octa-(silsesquioxane) $H_8Si_8O_{12}$ is the smallest member of the oligomeric $(HSiO_{3/2})_n$, $n = 8, 10, 12, 14, 16$ and 18 molecules, all of them having nearly spherical shape. They can be synthesized by hydrolytic condensation of $HSiCl_3$ in acidic medium [1] and separated by size-exclusion chromatography [2]. The octahedral structure of $H_8Si_8O_{12}$ was first determined by LARSSON [3] and later by DAY *et al.* [4]. It was found that its silicon-oxygen skeleton is about the same as in $(CH_3)_8Si_8O_{12}$. The i.r. spectrum of $H_8Si_8O_{12}$, a molecule which possesses 78 vibrational degrees of freedom, is very simple. Between 4000 and 40 cm^{-1} it consists of six fundamental i.r. absorptions. The Raman spectrum which is slightly more complicated consists of 13 fundamental vibrations. Provisional assignment of the i.r. spectrum has been given previously [5]. The high symmetry of this molecule makes it very attractive to carry out a complete normal coordinate analysis in terms of symmetry coordinates. This analysis is the basis for other interesting studies on $X_8Si_8O_{12}$ molecules and opens the way for quantitatively investigating the higher members of the oligomeric $(HSiO_{3/2})_n$ molecules. The normal coordinate analysis for cubane [6] can be used as a guide to introduce the internal coordinates. As we shall see, however, $H_8Si_8O_{12}$ is more complicated, so that correct orientation of the degenerate symmetry coordinates and elimination of redundant coordinates demands a systematic procedure. To generate the symmetry coordinates, this means the coordinates in terms of which the secular equation is factored to the maximum extent made possible by the symmetry [7], we apply a procedure described by GUSSONI and ZERBI [8], followed by some transformations described in this paper.

$H_8Si_8O_{12}$ has some resemblance to the double four ring (D4R) found in A-type zeolites. Infrared spectroscopy has provided very high quality information on zeolites, see Ref. [9] and references cited therein for examples. It is, however, in general very difficult to obtain a physical reliable force constant set for the zeolite framework. An interesting pseudo lattice study of the D4R unit has recently been carried out with the result that most of the calculated frequencies are in good agreement with the vibrational spectra in the 1200–250 cm^{-1} region [10]. Understanding the fundamental vibrations of the isolated $(HSiO_{3/2})_n$ molecules will help in such studies to classify modes which can be described as internal-coordinate frequencies and to distinguish them from modes which have to be treated as delocalized vibrations [11]. We therefore analyse the fundamental vibrations in terms of internal modes, namely $\nu(Si-H)$, $\nu(Si-O)$, $\delta(Si-H)$, $\delta(O-Si-O)$ and $\delta(Si-O-Si)$ and report the results of a potential energy distribution analysis [12] to describe the

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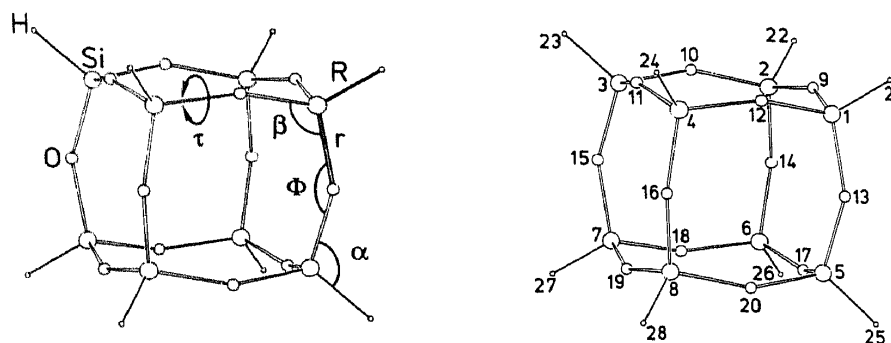* Author to whom correspondence should be addressed.

Fig. 1. Structure of $H_8Si_8O_{12}$ with internal coordinates and numbering of the atoms.

share of the individual symmetry coordinates in each normal vibration. The force constants, however, of the six i.r. active and of the 13 Raman active vibrations are given in terms of symmetry coordinates.

Internal Coordinates and Normal Vibrations

We start the analysis by assuming an octahedral structure for $H_8Si_8O_{12}$ with internal coordinates and numbering of the atoms as shown in Fig. 1. Bond lengths and bond angles collected in Table 1 have been taken from Ref. [3]. The numbering of the equivalent sets of internal coordinates is shown in Fig. 2. It is particularly convenient to use the linear combinations of the internal coordinates r, α, β, and τ collected in Table 2. The advantage of these linear combinations is that they break the equivalent sets into smaller equivalent sets, each of which is such that no more than one degenerate set occurs in any of the species [7]. Consider that the molecule consists of three symmetrically equivalent types of atoms. Each H atom is equivalent to the other H atoms, the same is true for the O atoms as well as for the Si atoms.

The 78 vibrational degrees of freedom of the octahedral $H_8Si_8O_{12}$ correspond to the following irreducible representations of the O_h group:

$$\Gamma_{\text{vib}} = 3A_{1g} + A_{2g} + 4E_g + 3T_{1g} + 6T_{2g} + 3A_{2u} + 3E_u + 6T_{1u} + 4T_{2u}.$$

From this follows that the molecule possesses 33 different fundamental modes. Out of them the six $T_{1u} \leftarrow A_{1g}$ transitions are i.r. active, the 13 $A_{1g} \leftarrow A_{1g}$, $E_g \leftarrow A_{1g}$ and $T_{2g} \leftarrow A_{1g}$ transitions are Raman active while the remaining 14 vibrations are inactive.

Table 1. Bond lengths and bond angles [3], values in parentheses from [19]

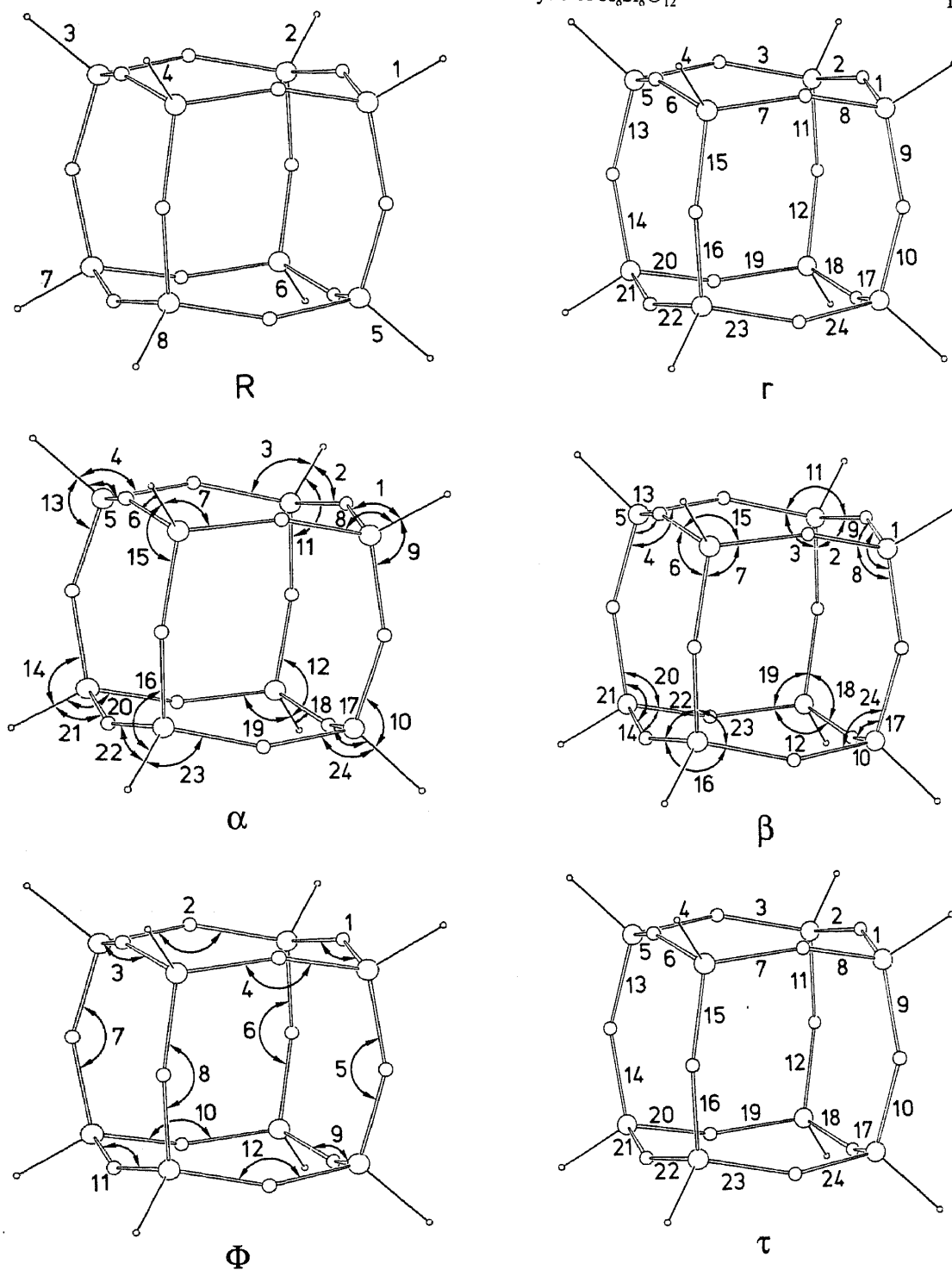| Coordinate	Value	
R(Si–H)	1.475 Å	(1.316 Å)
r(Si–O)	1.659 Å	(1.617 Å)
α(O–Si–H)	112.2°	(109.5°)
β(O–Si–O)	106.6°	(109.4°)
Φ(Si–O–Si)	153.9°	(148.5°)

Fig. 2. Numbering of the internal coordinates of H$_8$Si$_8$O$_{12}$.

Table 2. Definition of internal coordinates

R	$r(\pm)$	$\alpha(\pm)$	$\beta(\pm)$	Φ	$\tau(\pm)$
R_1	$r(\pm)_1 = r_1 \pm r_2$	$\alpha(\pm)_1 = \alpha_1 \pm \alpha_2$	$\beta(\pm)_1 = \beta_1 \pm \beta_6$	Φ_1	$\tau(\pm)_1 = \tau_1 \pm \tau_2$
R_2	$r(\pm)_2 = r_3 \pm r_4$	$\alpha(\pm)_2 = \alpha_3 \pm \alpha_4$	$\beta(\pm)_2 = \beta_2 \pm \beta_5$	Φ_2	$\tau(\pm)_2 = \tau_3 \pm \tau_4$
R_3	$r(\pm)_3 = r_5 \pm r_6$	$\alpha(\pm)_3 = \alpha_5 \pm \alpha_6$	$\beta(\pm)_3 = \beta_3 \pm \beta_8$	Φ_3	$\tau(\pm)_3 = \tau_5 \pm \tau_6$
R_4	$r(\pm)_4 = r_7 \pm r_8$	$\alpha(\pm)_4 = \alpha_7 \pm \alpha_8$	$\beta(\pm)_4 = \beta_4 \pm \beta_7$	Φ_4	$\tau(\pm)_4 = \tau_7 \pm \tau_8$
R_5	$r(\pm)_5 = r_9 \pm r_{10}$	$\alpha(\pm)_5 = \alpha_9 \pm \alpha_{10}$	$\beta(\pm)_5 = \beta_9 \pm \beta_{10}$	Φ_5	$\tau(\pm)_5 = \tau_9 \pm \tau_{10}$
R_6	$r(\pm)_6 = r_{11} \pm r_{12}$	$\alpha(\pm)_6 = \alpha_{11} \pm \alpha_{12}$	$\beta(\pm)_6 = \beta_{11} \pm \beta_{12}$	Φ_6	$\tau(\pm)_6 = \tau_{11} \pm \tau_{12}$
R_7	$r(\pm)_7 = r_{13} \pm r_{14}$	$\alpha(\pm)_7 = \alpha_{13} \pm \alpha_{14}$	$\beta(\pm)_7 = \beta_{13} \pm \beta_{14}$	Φ_7	$\tau(\pm)_7 = \tau_{13} \pm \tau_{14}$
R_8	$r(\pm)_8 = r_{15} \pm r_{16}$	$\alpha(\pm)_8 = \alpha_{15} \pm \alpha_{16}$	$\beta(\pm)_8 = \beta_{15} \pm \beta_{16}$	Φ_8	$\tau(\pm)_8 = \tau_{15} \pm \tau_{16}$
	$r(\pm)_9 = r_{17} \pm r_{18}$	$\alpha(\pm)_9 = \alpha_{17} \pm \alpha_{18}$	$\beta(\pm)_9 = \beta_{17} \pm \beta_{22}$	Φ_9	$\tau(\pm)_9 = \tau_{17} \pm \tau_{18}$
	$r(\pm)_{10} = r_{19} \pm r_{20}$	$\alpha(\pm)_{10} = \alpha_{19} \pm \alpha_{20}$	$\beta(\pm)_{10} = \beta_{18} \pm \beta_{21}$	Φ_{10}	$\tau(\pm)_{10} = \tau_{19} \pm \tau_{20}$
	$r(\pm)_{11} = r_{21} \pm r_{22}$	$\alpha(\pm)_{11} = \alpha_{21} \pm \alpha_{22}$	$\beta(\pm)_{11} = \beta_{19} \pm \beta_{24}$	Φ_{11}	$\tau(\pm)_{11} = \tau_{21} \pm \tau_{22}$
	$r(\pm)_{12} = r_{23} \pm r_{24}$	$\alpha(\pm)_{12} = \alpha_{23} \pm \alpha_{24}$	$\beta(\pm)_{12} = \beta_{20} \pm \beta_{23}$	Φ_{12}	$\tau(\pm)_{12} = \tau_{23} \pm \tau_{24}$

In order to find the symmetry coordinates we first have to calculate the irreducible representations generated by the equivalent sets of internal coordinates in Table 2. Standard procedures [7] lead to:

$$\Gamma_R = A_{1g} + T_{2g} + A_{2u} + T_{1u}$$

$$\Gamma_{r^+} = A_{1g} + E_g + T_{2g} + T_{1u} + T_{2u}$$

$$\Gamma_{r^-} = T_{1g} + T_{2g} + A_{2u} + E_u + T_{1u}$$

$$\Gamma_{a^+} = A_{1g} + E_g + T_{2g} + T_{1u} + T_{2u}$$

$$\Gamma_{a^-} = T_{1g} + T_{2g} + A_{2u} + E_u + T_{1u}$$

$$\Gamma_{\beta^+} = A_{1g} + E_g + T_{2g} + T_{1u} + T_{2u}$$

$$\Gamma_{\beta^-} = T_{1g} + T_{2g} + A_{2u} + E_u + T_{1u}$$

$$\Gamma_\Phi = A_{1g} + E_g + T_{2g} + T_{1u} + T_{2u}$$

$$\Gamma_{\tau^+} = T_{1g} + T_{2g} + A_{1u} + E_u + T_{2u}$$

$$\Gamma_{\tau^-} = A_{2g} + E_g + T_{1g} + T_{1u} + T_{2u}.$$

The sum Γ_{int} of these representations is of dimension 116. This means that 38 of them are redundant. The difference between Γ_{int} and Γ_{vib} corresponds to the redundant representations Γ_{red}:

$$\Gamma_{int} = 5A_{1g} + A_{2g} + 5E_g + 5T_{1g} + 9T_{2g} + A_{1u} + 4A_{2u} + 4E_u + 9T_{1u} + 6T_{2u}$$

$$\Gamma_{vib} = 3A_{1g} + A_{2g} + 4E_g + 3T_{1g} + 6T_{2g} + 3A_{2u} + 3E_u + 6T_{1u} + 4T_{2u}$$

$$\Gamma_{red} = 2A_{1g} + E_g + 2T_{1g} + 3T_{2g} + A_{1u} + A_{2u} + E_u + 3T_{1u} + 2T_{2u}.$$

Some of the redundant coordinates can easily be eliminated, taking into account that the sets of internal coordinates are not equivalent to each other. For example Γ_{r^+} is part of Γ_{red} and can therefore be eliminated. Γ_{r^-} has to be kept, however, because it is the only set containing an A_{2g} species. Another possibility would be to eliminate both, Γ_{r^+} and Γ_Φ resulting in

$$\Gamma_{red} - \Gamma_{r^+} - \Gamma_\Phi = A_{1g} + T_{1g} + T_{2g} + A_{2u} + 2T_{1u}.$$

After this partial success it is, however, not clear how the remaining problem should be solved. We therefore have to proceed in a more systematic way.

CONSTRUCTION OF INTERNAL SYMMETRY COORDINATES

While treating the problems of molecular vibrations, the factorization of the secular equation may be helpful. The so-called symmetry coordinates which factor the secular equation are generally built by the Wigner projection operator [7], a procedure which has been applied to construct the symmetry coordinates of the i.r. active vibrations of $H_8Si_8O_{12}$ as reported in [5]. In order to solve the whole problem, however, this method cannot easily be applied to such a large molecule. The starting of a powerful technique described by GUSSONI and ZERBI [8] consists in diagonalizing the Wilson **g** matrix.

For a molecule built of N atoms, the vector of 3N cartesian coordinates is defined as

$$X = (x_1, y_1, z_1, \ldots, x_N, y_N, z_N) \tag{1}$$

and the vector of internal coordinates is defined as

$$I = (i_1, i_2, \ldots, i_{3N-6}). \tag{2}$$

The matrix B transforms the cartesian coordinates X into the internal coordinates I:

$$I = BX. \tag{3}$$

The g matrix can be calculated as

$$g = BM^{-1}B^T \tag{4}$$

where M^{-1} is a diagonal matrix whose components are the reciprocal atomic masses, each of them repeated three times to account for motions in the three-dimensional space. Let g be diagonalized

$$gD = D\Gamma. \tag{5}$$

D is unitary since g is hermitian. GUSSONI and ZERBI [8] have shown that

$$\Sigma = D^T I \tag{6}$$

gives a completely reduced representation of the symmetry point group to which the molecule belongs and that, therefore, Σ are coordinates reflecting the symmetry of the molecule. It is perfectly possible to carry out the normal coordinate analysis by means of these coordinates. For molecules of such high symmetry as $H_8Si_8O_{12}$, the symmetry coordinates S have the advantage that they are much simpler and therefore more useful to define the potential energy function. It is therefore worthwhile to search for a matrix Δ which transforms Σ into S:

$$S = \Delta\Sigma. \tag{7}$$

Transformation (7) can be carried out as follows. The Σ coordinates, including the redundant ones, are sorted according to the magnitude of the eigenvalues. In general, the Σ will be mixtures of internal coordinates belonging to different sets of equivalent coordinates. Linear operations always allow to split them so, that each of the resulting coordinates will contain non-zero contributions only for a single set of equivalent internal coordinates. After this procedure appropriate rotation and normalization lead directly to the symmetry coordinates S.

In the case of $H_8Si_8O_{12}$ this procedure results in 116 symmetry coordinates, 38 of which are redundant. We have several possibilities to choose the non-redundant coordinates and it is known that the potential energy distribution for classifying vibrational modes is related to the type of coordinates used in setting up the vibrational problem [13]. The criteria we apply are to keep those coordinates which are (a) easiest to visualize and (b) lead to the simplest expression for the potential energy function. Keeping this in mind the elimination of the redundant coordinates has been carried out as described in Ref. [7].

It is useful to know the redundant coordinates. We therefore report in Table 3 the set of linearly independent, normalized symmetry coordinates and in Table 4 the corresponding redundant coordinates.

INFRARED AND RAMAN ACTIVE VIBRATIONS

To analyse the i.r. active fundamental modes we have to consider the T_{1u} symmetry coordinates S_{24}, S_{25}, S_{26}, S_{27}, S_{28} and S_{29}. The simplest realistic approximation to describe the potential energy function of the harmonic T_{1u} modes is

$$2V_{T_{1u}} = \sum_{n=24}^{29} F_{nn}S_{nn}^2. \tag{8}$$

The eigenvalue problem

$$|G_{T_{1u}}F_{T_{1u}} - \lambda E| = 0 \tag{9}$$

Table 3. Set of independent and normalized symmetry coordinates for $H_8Si_8O_{12}$

A_{1g}

S_1 $1/\sqrt{8}(R_1 + R_2 + R_3 + R_4 + R_5 + R_6 + R_7 + R_8)$

S_2 $1/\sqrt{24}(r_1 + r_2 + r_3 + r_4 + r_5 + r_6 + r_7 + r_8 + r_9 + r_{10} + r_{11} + r_{12}$
$+ r_{13} + r_{14} + r_{15} + r_{16} + r_{17} + r_{18} + r_{19} + r_{20} + r_{21} + r_{22} + r_{23} + r_{24})$

S_3 $1/\sqrt{24}(\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 + \alpha_5 + \alpha_6 + \alpha_7 + \alpha_8 + \alpha_9 + \alpha_{10} + \alpha_{11} + \alpha_{12}$
$+ \alpha_{13} + \alpha_{14} + \alpha_{15} + \alpha_{16} + \alpha_{17} + \alpha_{18} + \alpha_{19} + \alpha_{20} + \alpha_{21} + \alpha_{22} + \alpha_{23} + \alpha_{24})$

A_{2g}

S_4 $1/\sqrt{24}(\tau_1 - \tau_2 - \tau_3 + \tau_4 + \tau_5 - \tau_6 - \tau_7 + \tau_8 + \tau_9 - \tau_{10} - \tau_{11} + \tau_{12}$
$+ \tau_{13} - \tau_{14} - \tau_{15} + \tau_{16} - \tau_{17} + \tau_{18} + \tau_{19} - \tau_{20} - \tau_{21} + \tau_{22} + \tau_{23} - \tau_{24})$

E_g

S_{5a} $1/\sqrt{48}(r_1 + r_2 + r_3 + r_4 + r_5 + r_6 + r_7 + r_8 - 2r_9 - 2r_{10} - 2r_{11} - 2r_{12}$
$- 2r_{13} - 2r_{14} - 2r_{15} - 2r_{16} + r_{17} + r_{18} + r_{19} + r_{20} + r_{21} + r_{22} + r_{23} + r_{24})$

S_{5b} $1/4(r_1 + r_2 - r_3 - r_4 + r_5 + r_6 - r_7 - r_8 + r_{17} + r_{18} - r_{19} - r_{20} + r_{21} + r_{22} - r_{23} - r_{24})$

S_{6a} $1/\sqrt{48}(\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 + \alpha_5 + \alpha_6 + \alpha_7 + \alpha_8 - 2\alpha_9 - 2\alpha_{10} - 2\alpha_{11} - 2\alpha_{12}$
$- 2\alpha_{13} - 2\alpha_{14} - 2\alpha_{15} - 2\alpha_{16} + \alpha_{17} + \alpha_{18} + \alpha_{19} + \alpha_{20} + \alpha_{21} + \alpha_{22} + \alpha_{23} + \alpha_{24})$

S_{6b} $1/4(\alpha_1 + \alpha_2 - \alpha_3 - \alpha_4 + \alpha_5 + \alpha_6 - \alpha_7 - \alpha_8 + \alpha_{17} + \alpha_{18} - \alpha_{19} - \alpha_{20} + \alpha_{21} + \alpha_{22} - \alpha_{23} - \alpha_{24})$

S_{7a} $1/\sqrt{48}(\beta_1 + \beta_2 + \beta_3 + \beta_4 + \beta_5 + \beta_6 + \beta_7 + \beta_8 - 2\beta_9 - 2\beta_{10} - 2\beta_{11} - 2\beta_{12}$
$- 2\beta_{13} - 2\beta_{14} - 2\beta_{15} - 2\beta_{16} + \beta_{17} + \beta_{18} + \beta_{19} + \beta_{20} + \beta_{21} + \beta_{22} + \beta_{23} + \beta_{24})$

S_{7b} $1/4(-\beta_1 - \beta_2 + \beta_3 + \beta_4 - \beta_5 - \beta_6 + \beta_7 + \beta_8 - \beta_{17} - \beta_{18} + \beta_{19} + \beta_{20} - \beta_{21} - \beta_{22} + \beta_{23} + \beta_{24})$

S_{8a} $1/\sqrt{24}(\Phi_1 + \Phi_2 + \Phi_3 + \Phi_4 - 2\Phi_5 - 2\Phi_6 - 2\Phi_7 - 2\Phi_8 + \Phi_9 + \Phi_{10} + \Phi_{11} + \Phi_{12})$

S_{8b} $1/\sqrt{8}(\Phi_1 - \Phi_2 + \Phi_3 - \Phi_4 + \Phi_9 - \Phi_{10} + \Phi_{11} - \Phi_{12})$

T_{1g}

S_{9a} $1/4(r_1 - r_2 - r_5 + r_6 - r_9 + r_{10} + r_{11} - r_{12} + r_{13} - r_{14} - r_{15} + r_{16} - r_{17} + r_{18} + r_{21} - r_{22})$

S_{9b} $1/4(r_3 - r_4 - r_7 + r_8 - r_9 + r_{10} - r_{11} + r_{12} + r_{13} - r_{14} + r_{15} - r_{16} - r_{19} + r_{20} + r_{23} - r_{24})$

S_{9c} $1/4(r_1 - r_2 + r_3 - r_4 + r_5 - r_6 + r_7 - r_8 + r_{17} - r_{18} + r_{19} - r_{20} + r_{21} - r_{22} + r_{23} - r_{24})$

S_{10a} $1/4(\alpha_1 - \alpha_2 - \alpha_5 + \alpha_6 - \alpha_9 + \alpha_{10} + \alpha_{11} - \alpha_{12} + \alpha_{13} - \alpha_{14} - \alpha_{15} + \alpha_{16} - \alpha_{17} + \alpha_{18} + \alpha_{21} - \alpha_{22})$

S_{10b} $1/4(\alpha_3 - \alpha_4 - \alpha_7 + \alpha_8 - \alpha_9 + \alpha_{10} - \alpha_{11} + \alpha_{12} + \alpha_{13} - \alpha_{14} + \alpha_{15} - \alpha_{16} - \alpha_{19} + \alpha_{20} + \alpha_{23} - \alpha_{24})$

S_{10c} $1/4(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6 + \alpha_7 - \alpha_8 + \alpha_{17} - \alpha_{18} + \alpha_{19} - \alpha_{20} + \alpha_{21} - \alpha_{22} + \alpha_{23} - \alpha_{24})$

S_{11a} $1/4(\beta_3 + \beta_4 - \beta_7 - \beta_8 + \beta_9 - \beta_{10} - \beta_{11} + \beta_{12} - \beta_{13} + \beta_{14} + \beta_{15} - \beta_{16} - \beta_{19} - \beta_{20} + \beta_{23} + \beta_{24})$

S_{11b} $1/4(-\beta_1 - \beta_2 + \beta_5 + \beta_6 + \beta_9 - \beta_{10} + \beta_{11} - \beta_{12} - \beta_{13} + \beta_{14} - \beta_{15} + \beta_{16} + \beta_{17} + \beta_{18} - \beta_{21} - \beta_{22})$

S_{11c} $1/4(\beta_1 - \beta_2 + \beta_3 - \beta_4 + \beta_5 - \beta_6 + \beta_7 - \beta_8 + \beta_{17} - \beta_{18} + \beta_{19} - \beta_{20} + \beta_{21} - \beta_{22} + \beta_{23} - \beta_{24})$

T_{2g}

S_{12a} $1/\sqrt{8}(R_1 - R_2 + R_3 - R_4 + R_5 - R_6 + R_7 - R_8)$

S_{12b} $1/\sqrt{8}(-R_1 - R_2 + R_3 + R_4 + R_5 + R_6 - R_7 - R_8)$

S_{12c} $1/\sqrt{8}(R_1 - R_2 - R_3 + R_4 - R_5 + R_6 + R_7 - R_8)$

S_{13a} $1/\sqrt{8}(r_9 + r_{10} - r_{11} - r_{12} + r_{13} + r_{14} - r_{15} - r_{16})$

S_{13b} $1/\sqrt{8}(-r_1 - r_2 + r_5 + r_6 + r_{17} + r_{18} - r_{21} - r_{22})$

S_{13c} $1/\sqrt{8}(-r_3 - r_4 + r_7 + r_8 + r_{19} + r_{20} - r_{23} - r_{24})$

S_{14a} $1/4(r_1 - r_2 - r_3 + r_4 + r_5 - r_6 - r_7 + r_8 + r_{17} - r_{18} - r_{19} + r_{20} + r_{21} - r_{22} - r_{23} + r_{24})$

S_{14b} $1/4(-r_3 + r_4 + r_7 - r_8 - r_9 + r_{10} - r_{11} + r_{12} + r_{13} - r_{14} + r_{15} - r_{16} + r_{19} - r_{20} - r_{23} + r_{24})$

S_{14c} $1/4(r_1 - r_2 - r_5 + r_6 + r_9 - r_{10} - r_{11} + r_{12} - r_{13} + r_{14} + r_{15} - r_{16} - r_{17} + r_{18} + r_{21} - r_{22})$

S_{15a} $1/\sqrt{8}(\alpha_9 + \alpha_{10} - \alpha_{11} - \alpha_{12} + \alpha_{13} + \alpha_{14} - \alpha_{15} - \alpha_{16})$

S_{15b} $1/\sqrt{8}(-\alpha_1 - \alpha_2 + \alpha_5 + \alpha_6 + \alpha_{17} + \alpha_{18} - \alpha_{21} - \alpha_{22})$

S_{15c} $1/\sqrt{8}(-\alpha_3 - \alpha_4 + \alpha_7 + \alpha_8 + \alpha_{19} + \alpha_{20} - \alpha_{23} - \alpha_{24})$

S_{16a} $1/\sqrt{8}(\beta_9 + \beta_{10} - \beta_{11} - \beta_{12} + \beta_{13} + \beta_{14} - \beta_{15} - \beta_{16})$

S_{16b} $1/\sqrt{8}(-\beta_3 + \beta_4 + \beta_7 - \beta_8 + \beta_{19} - \beta_{20} - \beta_{23} + \beta_{24})$

S_{16c} $1/\sqrt{8}(\beta_1 - \beta_2 - \beta_5 + \beta_6 - \beta_{17} + \beta_{18} + \beta_{21} - \beta_{22})$

S_{17a} $1/4(\beta_1 - \beta_2 - \beta_3 + \beta_4 + \beta_5 - \beta_6 - \beta_7 + \beta_8 + \beta_{17} - \beta_{18} - \beta_{19} + \beta_{20} + \beta_{21} - \beta_{22} - \beta_{23} + \beta_{24})$

S_{17b} $1/4(-\beta_1 - \beta_2 + \beta_5 + \beta_6 - \beta_9 + \beta_{10} - \beta_{11} + \beta_{12} + \beta_{13} - \beta_{14} + \beta_{15} - \beta_{16} + \beta_{17} + \beta_{18} - \beta_{21} - \beta_{22})$

S_{17c} $1/4(-\beta_3 - \beta_4 + \beta_7 + \beta_8 + \beta_9 - \beta_{10} - \beta_{11} + \beta_{12} - \beta_{13} + \beta_{14} + \beta_{15} - \beta_{16} + \beta_{19} + \beta_{20} - \beta_{23} - \beta_{24})$

A_{2u}

S_{18} $1/\sqrt{8}(R_1 - R_2 + R_3 - R_4 - R_5 + R_6 - R_7 + R_8)$

S_{19} $1/\sqrt{24}(r_1 - r_2 - r_3 + r_4 + r_5 - r_6 - r_7 + r_8 + r_9 - r_{10} - r_{11} + r_{12}$
$+ r_{13} - r_{14} - r_{15} + r_{16} - r_{17} + r_{18} + r_{19} - r_{20} - r_{21} + r_{22} + r_{23} - r_{24})$

S_{20} $1/\sqrt{24}(\alpha_1 - \alpha_2 - \alpha_3 + \alpha_4 + \alpha_5 - \alpha_6 - \alpha_7 + \alpha_8 + \alpha_9 - \alpha_{10} - \alpha_{11} + \alpha_{12}$
$+ \alpha_{13} - \alpha_{14} - \alpha_{15} + \alpha_{16} - \alpha_{17} + \alpha_{18} + \alpha_{19} - \alpha_{20} - \alpha_{21} + \alpha_{22} + \alpha_{23} - \alpha_{24})$

is solved by standard methods [14]. Numerical analysis leads to the force constants collected in Table 5. Comparison of the observed and the calculated vibrational frequencies reported in Table 6 shows that Eqn (8) is sufficient to describe the

Table 3 (continued)

E_u

S_{21a} $1/\sqrt{48}(r_1 - r_2 - r_3 + r_4 + r_5 - r_6 - r_7 + r_8 - 2r_9 + 2r_{10} + 2r_{11} - 2r_{12}$
$- 2r_{13} + 2r_{14} + 2r_{15} - 2r_{16} - r_{17} + r_{18} + r_{19} - r_{20} - r_{21} + r_{22} + r_{23} - r_{24})$

S_{21b} $1/4(r_1 - r_2 + r_3 - r_4 + r_5 - r_6 + r_7 - r_8 - r_{17} + r_{18} - r_{19} + r_{20} - r_{21} + r_{22} - r_{23} + r_{24})$

S_{22a} $1/\sqrt{48}(\alpha_1 - \alpha_2 - \alpha_3 + \alpha_4 + \alpha_5 - \alpha_6 - \alpha_7 + \alpha_8 - 2\alpha_9 + 2\alpha_{10} + 2\alpha_{11} - 2\alpha_{12}$
$- 2\alpha_{13} + 2\alpha_{14} + 2\alpha_{15} - 2\alpha_{16} - \alpha_{17} + \alpha_{18} + \alpha_{19} - \alpha_{20} - \alpha_{21} + \alpha_{22} + \alpha_{23} - \alpha_{24})$

S_{22b} $1/4(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6 + \alpha_7 - \alpha_8 - \alpha_{17} + \alpha_{18} - \alpha_{19} + \alpha_{20} - \alpha_{21} + \alpha_{22} - \alpha_{23} + \alpha_{24})$

S_{23a} $1/\sqrt{48}(\beta_1 - \beta_2 - \beta_3 + \beta_4 + \beta_5 - \beta_6 - \beta_7 + \beta_8 - 2\beta_9 + 2\beta_{10} + 2\beta_{11} - 2\beta_{12}$
$- 2\beta_{13} + 2\beta_{14} + 2\beta_{15} - 2\beta_{16} - \beta_{17} + \beta_{18} + \beta_{19} - \beta_{20} - \beta_{21} + \beta_{22} + \beta_{23} - \beta_{24})$

S_{23b} $1/4(-\beta_1 + \beta_2 - \beta_3 + \beta_4 - \beta_5 + \beta_6 - \beta_7 + \beta_8 + \beta_{17} - \beta_{18} + \beta_{19} - \beta_{20} + \beta_{21} - \beta_{22} + \beta_{23} - \beta_{24})$

T_{1u}

S_{24a} $1/\sqrt{8}(R_1 + R_2 + R_3 + R_4 - R_5 - R_6 - R_7 - R_8)$

S_{24b} $1/\sqrt{8}(R_1 + R_2 - R_3 - R_4 + R_5 + R_6 - R_7 - R_8)$

S_{24c} $1/\sqrt{8}(R_1 - R_2 - R_3 + R_4 + R_5 - R_6 - R_7 + R_8)$

S_{25a} $1/4(r_1 + r_2 + r_3 + r_4 + r_5 + r_6 + r_7 + r_8 - r_{17} - r_{18} - r_{19} - r_{20} - r_{21} - r_{22} - r_{23} - r_{24})$

S_{25b} $1/4(r_1 + r_2 - r_5 - r_6 + r_9 + r_{10} + r_{11} + r_{12} - r_{13} - r_{14} - r_{15} - r_{16} + r_{17} + r_{18} - r_{21} - r_{22})$

S_{25c} $1/4(-r_3 - r_4 + r_7 + r_8 + r_9 + r_{10} - r_{11} - r_{12} - r_{13} - r_{14} + r_{15} + r_{16} - r_{19} - r_{20} + r_{23} + r_{24})$

S_{26a} $1/\sqrt{8}(r_9 - r_{10} + r_{11} - r_{12} + r_{13} - r_{14} + r_{15} - r_{16})$

S_{26b} $1/\sqrt{8}(r_3 - r_4 - r_7 + r_8 + r_{19} - r_{20} - r_{23} + r_{24})$

S_{26c} $1/\sqrt{8}(r_1 - r_2 - r_5 + r_6 + r_{17} - r_{18} - r_{21} + r_{22})$

S_{27a} $1/\sqrt{8}(\alpha_9 - \alpha_{10} + \alpha_{11} - \alpha_{12} + \alpha_{13} - \alpha_{14} + \alpha_{15} - \alpha_{16})$

S_{27b} $1/\sqrt{8}(\alpha_3 - \alpha_4 - \alpha_7 + \alpha_8 + \alpha_{19} - \alpha_{20} - \alpha_{23} + \alpha_{24})$

S_{27c} $1/\sqrt{8}(\alpha_1 - \alpha_2 - \alpha_5 + \alpha_6 + \alpha_{17} - \alpha_{18} - \alpha_{21} + \alpha_{22})$

S_{28a} $1/4(\beta_1 + \beta_2 + \beta_3 + \beta_4 + \beta_5 + \beta_6 + \beta_7 + \beta_8 - \beta_{17} - \beta_{18} - \beta_{19} - \beta_{20} - \beta_{21} - \beta_{22} - \beta_{23} - \beta_{24})$

S_{28b} $1/4(\beta_3 - \beta_4 - \beta_7 + \beta_8 + \beta_9 + \beta_{10} + \beta_{11} + \beta_{12} - \beta_{13} - \beta_{14} - \beta_{15} - \beta_{16} + \beta_{19} - \beta_{20} - \beta_{23} + \beta_{24})$

S_{28c} $1/4(\beta_1 - \beta_2 - \beta_5 + \beta_6 + \beta_9 + \beta_{10} - \beta_{11} - \beta_{12} - \beta_{13} - \beta_{14} + \beta_{15} + \beta_{16} + \beta_{17} - \beta_{18} - \beta_{21} + \beta_{22})$

S_{29a} $1/\sqrt{8}(\beta_9 - \beta_{10} + \beta_{11} - \beta_{12} + \beta_{13} - \beta_{14} + \beta_{15} - \beta_{16})$

S_{29b} $1/\sqrt{8}(\beta_1 + \beta_2 - \beta_5 - \beta_6 + \beta_{17} + \beta_{18} - \beta_{21} - \beta_{22})$

S_{29c} $1/\sqrt{8}(-\beta_3 - \beta_4 + \beta_7 + \beta_8 - \beta_{19} - \beta_{20} + \beta_{23} + \beta_{24})$

T_{2u}

S_{30a} $1/4(r_1 + r_2 - r_3 - r_4 + r_5 + r_6 - r_7 - r_8 - r_{17} - r_{18} + r_{19} + r_{20} - r_{21} - r_{22} + r_{23} + r_{24})$

S_{30b} $1/4(r_1 + r_2 - r_5 - r_6 - r_9 - r_{10} - r_{11} - r_{12} + r_{13} + r_{14} + r_{15} + r_{16} + r_{17} + r_{18} - r_{21} - r_{22})$

S_{30c} $1/4(r_3 + r_4 - r_7 - r_8 + r_9 + r_{10} - r_{11} - r_{12} - r_{13} - r_{14} + r_{15} + r_{16} + r_{19} + r_{20} - r_{23} - r_{24})$

S_{31a} $1/4(\alpha_1 + \alpha_2 - \alpha_3 - \alpha_4 + \alpha_5 + \alpha_6 - \alpha_7 - \alpha_8 - \alpha_{17} - \alpha_{18} + \alpha_{19} + \alpha_{20} - \alpha_{21} - \alpha_{22} + \alpha_{23} + \alpha_{24})$

S_{31b} $1/4(\alpha_1 + \alpha_2 - \alpha_5 - \alpha_6 - \alpha_9 - \alpha_{10} - \alpha_{11} - \alpha_{12} + \alpha_{13} + \alpha_{14} + \alpha_{15} + \alpha_{16} + \alpha_{17} + \alpha_{18} - \alpha_{21} - \alpha_{22})$

S_{31c} $1/4(\alpha_3 + \alpha_4 - \alpha_7 - \alpha_8 + \alpha_9 + \alpha_{10} - \alpha_{11} - \alpha_{12} - \alpha_{13} - \alpha_{14} + \alpha_{15} + \alpha_{16} + \alpha_{19} + \alpha_{20} - \alpha_{23} - \alpha_{24})$

S_{32a} $1/4(\beta_1 + \beta_2 - \beta_3 - \beta_4 + \beta_5 + \beta_6 - \beta_7 - \beta_8 - \beta_{17} - \beta_{18} + \beta_{19} + \beta_{20} - \beta_{21} - \beta_{22} + \beta_{23} + \beta_{24})$

S_{32b} $1/4(-\beta_3 + \beta_4 + \beta_7 - \beta_8 + \beta_9 + \beta_{10} + \beta_{11} + \beta_{12} - \beta_{13} - \beta_{14} - \beta_{15} - \beta_{16} - \beta_{19} + \beta_{20} + \beta_{23} - \beta_{24})$

S_{32c} $1/4(\beta_1 - \beta_2 - \beta_5 + \beta_6 - \beta_9 - \beta_{10} + \beta_{11} + \beta_{12} + \beta_{13} + \beta_{14} - \beta_{15} - \beta_{16} + \beta_{17} - \beta_{18} - \beta_{21} + \beta_{22})$

S_{33a} $1/\sqrt{8}(\Phi_1 - \Phi_2 + \Phi_3 - \Phi_4 - \Phi_9 + \Phi_{10} - \Phi_{11} + \Phi_{12})$

S_{33b} $1/\sqrt{8}(\Phi_1 - \Phi_3 - \Phi_5 - \Phi_6 + \Phi_7 + \Phi_8 + \Phi_9 - \Phi_{11})$

S_{33c} $1/\sqrt{8}(\Phi_2 - \Phi_4 + \Phi_5 - \Phi_6 - \Phi_7 + \Phi_8 + \Phi_{10} - \Phi_{12})$

experimental observations. The presented solution is the only one which by means of Eqn (8) allows quantitative description of the experimental data. Mixing of the symmetry coordinates in the normal vibrations can be analysed by calculating the potential energy distribution (PED) according to [12, 14]:

$$P_{ij} = \frac{F_{ii}L_{ij}^2}{\sum_i F_{ii}L_{ij}^2}. \tag{10}$$

The L matrix is defined by $S = LQ$ whereby Q are the normal coordinates. The results of this analysis in Table 6 show the % contribution of the symmetry coordinates to a certain normal mode. From the potential energy distribution (PED) analysis, it follows that ν_{24} to ν_{29} can be regarded as being one of the internal vibrations $\nu(Si-H)$, $\nu(Si-O)$,

$\delta(Si-H)$ or $\delta(O-Si-O)$. This makes it easy to compare them with vibrations observed in similar silicon compounds.

Out of the 13 Raman active fundamental vibrations, three are of A_{1g} symmetry, four are of E_g symmetry and the remaining six belong to the T_{2g} species of the O_h point group. Again the simplest realistic approximation for the potential energy function of the

Table 4. Set of independent and normalized redundant symmetry coordinates for $H_8Si_8O_{12}$

A_{1g}

S_{R1} $\quad 1/\sqrt{24}(\beta_1 + \beta_2 + \beta_3 + \beta_4 + \beta_5 + \beta_6 + \beta_7 + \beta_8 + \beta_9 + \beta_{10} + \beta_{11} + \beta_{12}$
$\quad\quad + \beta_{13} + \beta_{14} + \beta_{15} + \beta_{16} + \beta_{17} + \beta_{18} + \beta_{19} + \beta_{20} + \beta_{21} + \beta_{22} + \beta_{23} + \beta_{24})$

S_{R2} $\quad 1/\sqrt{12}(\Phi_1 + \Phi_2 + \Phi_3 + \Phi_4 + \Phi_5 + \Phi_6 + \Phi_7 + \Phi_8 + \Phi_9 + \Phi_{10} + \Phi_{11} + \Phi_{12})$

E_g

S_{R3a} $\quad 1/4(\tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6 + \tau_7 - \tau_8 - \tau_{17} + \tau_{18} - \tau_{19} + \tau_{20} - \tau_{21} + \tau_{22} - \tau_{23} + \tau_{24})$

S_{R3b} $\quad 1/\sqrt{48}(-\tau_1 + \tau_2 + \tau_3 - \tau_4 - \tau_5 + \tau_6 + \tau_7 - \tau_8 + 2\tau_9 - 2\tau_{10} - 2\tau_{11} + 2\tau_{12}$
$\quad\quad + 2\tau_{13} - 2\tau_{14} - 2\tau_{15} + 2\tau_{16} + \tau_{17} - \tau_{18} - \tau_{19} + \tau_{20} + \tau_{21} - \tau_{22} - \tau_{23} + \tau_{24})$

T_{1g}

S_{R4a} $\quad 1/4(\tau_1 + \tau_2 - \tau_5 - \tau_6 + \tau_9 + \tau_{10} + \tau_{11} + \tau_{12} - \tau_{13} - \tau_{14} - \tau_{15} - \tau_{16} + \tau_{17} + \tau_{18} - \tau_{21} - \tau_{22})$

S_{R4b} $\quad 1/4(\tau_3 + \tau_4 - \tau_7 - \tau_8 - \tau_9 - \tau_{10} + \tau_{11} + \tau_{12} + \tau_{13} + \tau_{14} - \tau_{15} - \tau_{16} + \tau_{19} + \tau_{20} - \tau_{23} - \tau_{24})$

S_{R4c} $\quad 1/4(-\tau_1 - \tau_2 - \tau_3 - \tau_4 - \tau_5 - \tau_6 - \tau_7 - \tau_8 + \tau_{17} + \tau_{18} + \tau_{19} + \tau_{20} + \tau_{21} + \tau_{22} + \tau_{23} + \tau_{24})$

S_{R5a} $\quad 1/\sqrt{8}(\tau_3 - \tau_4 - \tau_7 + \tau_8 + \tau_{19} - \tau_{20} - \tau_{23} + \tau_{24})$

S_{R5b} $\quad 1/\sqrt{8}(-\tau_1 + \tau_2 + \tau_5 - \tau_6 - \tau_{17} + \tau_{18} + \tau_{21} - \tau_{22})$

S_{R5c} $\quad 1/\sqrt{8}(-\tau_9 + \tau_{10} - \tau_{11} + \tau_{12} - \tau_{13} + \tau_{14} - \tau_{15} + \tau_{16})$

T_{2g}

S_{R6a} $\quad 1/4(\alpha_1 - \alpha_2 - \alpha_3 + \alpha_4 + \alpha_5 - \alpha_6 - \alpha_7 + \alpha_8 + \alpha_{17} - \alpha_{18} - \alpha_{19} + \alpha_{20} + \alpha_{21} - \alpha_{22} - \alpha_{23} + \alpha_{24})$

S_{R6b} $\quad 1/4(-\alpha_3 + \alpha_4 + \alpha_7 - \alpha_8 - \alpha_9 + \alpha_{10} - \alpha_{11} + \alpha_{12} + \alpha_{13} - \alpha_{14} + \alpha_{15} - \alpha_{16} + \alpha_{19} - \alpha_{20} - \alpha_{23} + \alpha_{24})$

S_{R6c} $\quad 1/4(\alpha_1 - \alpha_2 - \alpha_5 + \alpha_6 + \alpha_9 - \alpha_{10} - \alpha_{11} + \alpha_{12} - \alpha_{13} + \alpha_{14} + \alpha_{15} - \alpha_{16} - \alpha_{17} + \alpha_{18} + \alpha_{21} - \alpha_{22})$

S_{R7a} $\quad 1/2(\Phi_5 - \Phi_6 + \Phi_7 - \Phi_8)$

S_{R7b} $\quad 1/2(-\Phi_1 + \Phi_3 + \Phi_9 - \Phi_{11})$

S_{R7c} $\quad 1/2(-\Phi_2 + \Phi_4 + \Phi_{10} - \Phi_{12})$

S_{R8a} $\quad 1/4(\tau_1 + \tau_2 - \tau_3 - \tau_4 + \tau_5 + \tau_6 - \tau_7 - \tau_8 - \tau_{17} - \tau_{18} + \tau_{19} + \tau_{20} - \tau_{21} - \tau_{22} + \tau_{23} + \tau_{24})$

S_{R8b} $\quad 1/4(\tau_3 + \tau_4 - \tau_7 - \tau_8 + \tau_9 + \tau_{10} - \tau_{11} - \tau_{12} - \tau_{13} - \tau_{14} + \tau_{15} + \tau_{16} + \tau_{19} + \tau_{20} - \tau_{23} - \tau_{24})$

S_{R8c} $\quad 1/4(-\tau_1 - \tau_2 + \tau_5 + \tau_6 + \tau_9 + \tau_{10} + \tau_{11} + \tau_{12} - \tau_{13} - \tau_{14} - \tau_{15} - \tau_{16} - \tau_{17} - \tau_{18} + \tau_{21} + \tau_{22})$

A_{1u}

S_{R9} $\quad 1/\sqrt{24}(\tau_1 + \tau_2 + \tau_3 + \tau_4 + \tau_5 + \tau_6 + \tau_7 + \tau_8 + \tau_9 + \tau_{10} + \tau_{11} + \tau_{12}$
$\quad\quad + \tau_{13} + \tau_{14} + \tau_{15} + \tau_{16} + \tau_{17} + \tau_{18} + \tau_{19} + \tau_{20} + \tau_{21} + \tau_{22} + \tau_{23} + \tau_{24})$

A_{2u}

S_{R10} $\quad 1/\sqrt{24}(\beta_1 - \beta_2 - \beta_3 + \beta_4 + \beta_5 - \beta_6 - \beta_7 + \beta_8 + \beta_9 - \beta_{10} - \beta_{11} + \beta_{12}$
$\quad\quad + \beta_{13} - \beta_{14} - \beta_{15} + \beta_{16} - \beta_{17} + \beta_{18} + \beta_{19} - \beta_{20} - \beta_{21} + \beta_{22} + \beta_{23} - \beta_{24})$

E_u

S_{R11a} $\quad 1/4(\tau_1 + \tau_2 - \tau_3 - \tau_4 + \tau_5 + \tau_6 - \tau_7 - \tau_8 + \tau_{17} + \tau_{18} - \tau_{19} - \tau_{20} + \tau_{21} + \tau_{22} - \tau_{23} - \tau_{24})$

S_{R11b} $\quad 1/\sqrt{48}(-\tau_1 - \tau_2 - \tau_3 - \tau_4 - \tau_5 - \tau_6 - \tau_7 - \tau_8 + 2\tau_9 + 2\tau_{10} + 2\tau_{11} + 2\tau_{12}$
$\quad\quad + 2\tau_{13} + 2\tau_{14} + 2\tau_{15} + 2\tau_{16} - \tau_{17} - \tau_{18} - \tau_{19} - \tau_{20} - \tau_{21} - \tau_{22} - \tau_{23} - \tau_{24})$

T_{1u}

S_{R12a} $\quad 1/4(\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 + \alpha_5 + \alpha_6 + \alpha_7 + \alpha_8 - \alpha_{17} - \alpha_{18} - \alpha_{19} - \alpha_{20} - \alpha_{21} - \alpha_{22} - \alpha_{23} - \alpha_{24})$

S_{R12b} $\quad 1/4(\alpha_1 + \alpha_2 - \alpha_5 - \alpha_6 + \alpha_9 + \alpha_{10} + \alpha_{11} + \alpha_{12} - \alpha_{13} - \alpha_{14} - \alpha_{15} - \alpha_{16} + \alpha_{17} + \alpha_{18} - \alpha_{21} - \alpha_{22})$

S_{R12c} $\quad 1/4(-\alpha_3 - \alpha_4 + \alpha_7 + \alpha_8 + \alpha_9 + \alpha_{10} - \alpha_{11} - \alpha_{12} - \alpha_{13} - \alpha_{14} + \alpha_{15} + \alpha_{16} - \alpha_{19} - \alpha_{20} + \alpha_{23} + \alpha_{24})$

S_{R13a} $\quad 1/\sqrt{8}(\Phi_1 + \Phi_2 + \Phi_3 + \Phi_4 - \Phi_9 - \Phi_{10} - \Phi_{11} - \Phi_{12})$

S_{R13b} $\quad 1/\sqrt{8}(\Phi_1 - \Phi_3 + \Phi_5 + \Phi_6 - \Phi_7 - \Phi_8 + \Phi_9 - \Phi_{11})$

S_{R13c} $\quad 1/\sqrt{8}(-\Phi_2 + \Phi_4 + \Phi_5 - \Phi_6 - \Phi_7 + \Phi_8 - \Phi_{10} + \Phi_{12})$

S_{R14a} $\quad 1/4(\tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6 + \tau_7 - \tau_8 + \tau_{17} - \tau_{18} + \tau_{19} - \tau_{20} + \tau_{21} - \tau_{22} + \tau_{23} - \tau_{24})$

S_{R14b} $\quad 1/4(-\tau_1 + \tau_2 + \tau_5 - \tau_6 + \tau_9 - \tau_{10} - \tau_{11} + \tau_{12} - \tau_{13} + \tau_{14} + \tau_{15} - \tau_{16} + \tau_{17} - \tau_{18} - \tau_{21} + \tau_{22})$

S_{R14c} $\quad 1/4(\tau_3 - \tau_4 - \tau_7 + \tau_8 - \tau_9 + \tau_{10} - \tau_{11} + \tau_{12} + \tau_{13} - \tau_{14} + \tau_{15} - \tau_{16} - \tau_{19} + \tau_{20} + \tau_{23} - \tau_{24})$

T_{2u}

S_{R15a} $\quad 1/\sqrt{8}(\tau_9 + \tau_{10} - \tau_{11} - \tau_{12} + \tau_{13} + \tau_{14} - \tau_{15} - \tau_{16})$

S_{R15b} $\quad 1/\sqrt{8}(\tau_3 + \tau_4 - \tau_7 - \tau_8 - \tau_{19} - \tau_{20} + \tau_{23} + \tau_{24})$

S_{R15c} $\quad 1/\sqrt{8}(-\tau_1 - \tau_2 + \tau_5 + \tau_6 + \tau_{17} + \tau_{18} - \tau_{21} - \tau_{22})$

S_{R16a} $\quad 1/4(\tau_1 - \tau_2 - \tau_3 + \tau_4 + \tau_5 - \tau_6 - \tau_7 + \tau_8 + \tau_{17} - \tau_{18} - \tau_{19} + \tau_{20} + \tau_{21} - \tau_{22} - \tau_{23} + \tau_{24})$

S_{R16b} $\quad 1/4(-\tau_1 + \tau_2 + \tau_5 - \tau_6 - \tau_9 + \tau_{10} + \tau_{11} - \tau_{12} + \tau_{13} - \tau_{14} - \tau_{15} + \tau_{16} + \tau_{17} - \tau_{18} - \tau_{21} + \tau_{22})$

S_{R16c} $\quad 1/4(-\tau_3 + \tau_4 + \tau_7 - \tau_8 - \tau_9 + \tau_{10} - \tau_{11} + \tau_{12} + \tau_{13} - \tau_{14} + \tau_{15} - \tau_{16} + \tau_{19} - \tau_{20} - \tau_{23} + \tau_{24})$

Table 5. Force constants for the i.r. vibrations; values in parentheses have been calculated by means of structural data from [19]

Force constant	Value (mdyn Å^{-1})	(mdyn Å rad^{-2})
T_{1u}		
$F_{24,24}$	2.958 (2.959)	
$F_{25,25}$	5.439 (5.042)	
$F_{26,26}$	4.729 (4.718)	
$F_{27,27}$		0.871 (0.707)
$F_{28,28}$		1.526 (1.966)
$F_{29,29}$		1.372 (1.098)

Raman active modes is

$$2V_{A_{1g}, E_g, T_{2g}} = 2V_{A_{1g}} + 2V_{E_g} + 2V_{T_{2g}} = \sum_{n=1}^{3} F_{nn}S_{nn}^2 + \sum_{n=5}^{8} F_{nn}S_{nn}^2 + \sum_{n=12}^{17} F_{nn}S_{nn}^2. \quad (11)$$

Numerical analysis shows that this potential energy expression is sufficient with the exception of $2V_{E_g}$ where $F_{56} = F_{65} \neq 0$ has to be used.

A good simplified force field to describe the i.r. and the Raman active vibrations in terms of internal force constants can be expressed as follows:

A_{1g}	E_g	T_{2g}	T_{1u}
$F_{1,1} = f_R + 3f_{RR}$	$F_{5,5} = f_r + f_{rr} - f'_{rr}$	$F_{12,12} = f_R - f_{RR}$	$F_{24,24} = f_R + f_{RR}$
$F_{2,2} = f_r + f_{rr} + 2f'_{rr}$	$F_{6,6} = f_\alpha - f_{\alpha\alpha}$	$F_{13,13} = f_r + f_{rr}$	$F_{25,25} = f_r + f_{rr} + f'_{rr}$
$F_{3,3} = f_\alpha + 2f_{\alpha\alpha}$	$F_{7,7} = f_\beta - f_{\beta\beta}$	$F_{14,14} = f_r - f_{rr} + f'_{rr}$	$F_{26,26} = f_r - f_{rr}$
	$F_{8,8} = f_\Phi - 2f_{\Phi\Phi}$	$F_{15,15} = f_\alpha$	$F_{27,27} = f_\alpha$
		$F_{16,16} = f_\beta$	$F_{28,28} = f_\beta + f_{\beta\beta}$
		$F_{17,17} = f_\beta + f_{\beta\beta}$	$F_{29,29} = f_\beta. \quad (12)$

Having accepted this force field it is easy to express the force constants of the Raman active vibrations A_{1g}, E_g and T_{2g} in terms of those of the i.r. active modes:

A_{1g}	E_g	T_{2g}
$F_{1,1} = F_{24,24} + 2f_{RR}$	$F_{5,5} = F_{25,25} - 2f'_{rr}$	$F_{12,12} = F_{24,24} - 2f_{RR}$
$F_{2,2} = F_{25,25} + f'_{rr}$	$F_{6,6} = F_{27,27} - f_{\alpha\alpha}$	$F_{13,13} = F_{25,25} - f'_{rr}$
$F_{3,3} = F_{27,27} + 2f_{\alpha\alpha}$	$F_{7,7} = F_{29,29} - f_{\beta\beta}$	$F_{14,14} = F_{26,26} + f'_{rr}$
	$F_{8,8} = f_\Phi - 2f_{\Phi\Phi}$	$F_{15,15} = F_{27,27}$
		$F_{16,16} = F_{29,29}$
		$F_{17,17} = F_{28,28}. \quad (13)$

Table 6. Infrared active vibrations

Normal mode	Observed (cm^{-1})	Calculated (cm^{-1})	PED	Type
T_{1u}				
ν_{24}	2274.0	2274.0	100 S_{24}	$\nu(Si-H)$
ν_{25}	1140.0	1140.0	93 S_{26}	$\nu(Si-O)$
ν_{26}	878.0	878.0	92 S_{27}	$\delta(Si-H)$
ν_{27}	560.0	560.0	58 $S_{29} + 27 S_{25}$	$\delta(O-Si-O)$
ν_{28}	468.0	468.0	63 $S_{25} + 21 S_{29} + 14 S_{28}$	$\nu(Si-O)$
ν_{29}	399.0	399.0	77 $S_{28} + 17 S_{29}$	$\delta(O-Si-O)$

Table 7. Force constants for the Raman vibrations

Force constant	(mdyn Å^{-1})	Value (mdyn Å rad^{-2})	(mdyn rad^{-1})
A_{1g}			
$F_{1,1}$	3.032		
$F_{2,2}$	5.424		
$F_{3,3}$		1.316	
E_g			
$F_{5,5}$	5.161		
$F_{5,6} = F_{6,5}$			0.200
$F_{6,6}$		0.647	
$F_{7,7}$		1.353	
$F_{8,8}$		0.295	
T_{2g}			
$F_{12,12}$	2.988		
$F_{13,13}$	5.316		
$F_{14,14}$	4.700		
$F_{15,15}$		0.876	
$F_{16,16}$		1.369	
$F_{17,17}$		1.527	

Regarding the vibrations ν_3, ν_8, ν_{16} and ν_{17}, there is no good experimental data available. We have therefore made use of Eqn (13) together with the Raman data to calculate the results collected in Tables 7 and 8.

DISCUSSION

The normal coordinate analysis of the $H_8Si_8O_{12}$ molecule, which at first glance appears to be a difficult problem, leads to a clear description of the fundamental modes of this molecule. We conclude that the presented results can be regarded as a beginning to quantitatively describe larger silsesquioxanes and their corresponding inclusion compounds. A simple comparison of the vibrations observed in similar silicon compounds is made possible by the result of the potential energy distribution analysis that the

Table 8. Raman active vibrations

Normal mode	Observed* (cm^{-1})	Calculated (cm^{-1})	PED	Type
A_{1g}				
ν_1	2301.8	2301.8	100 S_1	$\nu(Si\text{–}H)$
ν_2	456.6	456.6	74 S_2 + 26 S_3	$\nu(Si\text{–}O)$
ν_3		393.0	74 S_3 + 26 S_2	$\delta(Si\text{–}H)$
E_g				
ν_5	932.4	932.4	87 S_6 + 12 S_5	$\delta(Si\text{–}H)$
ν_6	697.3	697.3	61 S_5 + 31 S_7	$\nu(Si\text{–}O)$
ν_7	500.0	500.0	68 S_7 + 25 S_5	$\delta(O\text{–}Si\text{–}O)$
ν_8		148.0	92 S_8	$\delta(Si\text{–}O\text{–}Si)$
T_{2g}				
ν_{12}	2285.4	2285.4	100 S_{12}	$\nu(Si\text{–}H)$
ν_{13}	1117.0	1117.0	83 S_{14} + 10 S_{15}	$\nu(Si\text{–}O)$
ν_{14}	891.1	891.1	83 S_{15} + 13 S_{14}	$\delta(Si\text{–}H)$
ν_{15}	610.0	610.0	76 S_{13} + 17 S_{17}	$\nu(Si\text{–}O)$
ν_{16}		341.0	80 S_{17} + 12 S_{13}	$\delta(O\text{–}Si\text{–}O)$
ν_{17}		194.0	92 S_{16}	$\delta(O\text{–}Si\text{–}O)$

* Unpublished FTIR Raman experiments.

Table 9. Comparison of Si–H vibrational frequencies

SiH_4[17]	Si_6H_{12}[18]	$H_8Si_8O_{12}$
	$\nu(Si-H)$	
A_1 2186.9 (R)	A_{1g} 2128(ax) (R)	A_{1g} 2301.8 (R)
	A_{1g} 2128(eq) (R)	
T_2 2189.2 (i.r.)		T_{2g} 2285.4 (R)
	E_g 2128(ax) (R)	
	E_g 2128(eq) (R)	T_{1u} 2274.0 (i.r.)
	A_{2u} 2120(ax) (i.r.)	
	A_{2u} 2120(eq) (i.r.)	
	E_u 2120(ax) (i.r.)	
	E_u 2120(eq) (i.r.)	
	$\delta(Si-H)$	
E 971.0 (R)	A_{1g} 515(eq) (R)	A_{1g} 393.0 (R)
	A_{1g} 377(ax) (R)	
T_2 913.5 (i.r.)		E_g 932.4 (R)
	E_g 893(eq) (R)	
	E_g 736(ax) (R)	T_{2g} 891.1 (R)
	E_g 655(eq) (R)	
	E_g 476(ax) (R)	T_{1u} 878.0 (i.r.)
	A_{2u} 384(eq) (i.r.)	
	A_{2u} 330(ax) (i.r.)	
	E_u 865(eq) (i.r.)	
	E_u 720(ax) (i.r.)	
	E_u 625(ax) (i.r.)	
	E_u 519(eq) (i.r.)	

fundamental modes can be described in terms of the internal vibrations $\nu(Si-H)$, $\nu(Si-O)$, $\delta(Si-H)$, $\delta(O-Si-O)$ and $\delta(Si-O-Si)$. SMITH [15] reported Si–H and Si–O i.r. frequencies in the region of $\nu(Si-H) = 2250-2100 \text{ cm}^{-1}$, $\delta(Si-H) = 950-800 \text{ cm}^{-1}$ and $\nu(Si-O) = 1125-1010 \text{ cm}^{-1}$ of silicon hydride and silicon oxide compounds. These data fit well with $\nu_{T_{1u}}(Si-H) = 2274 \text{ cm}^{-1}$, $\delta_{T_{1u}}(Si-H) = 878 \text{ cm}^{-1}$ and $\nu_{T_{1u}}(Si-O) = 1140 \text{ cm}^{-1}$ of $H_8Si_8O_{12}$. A very intense $\nu(Si-O)$ absorption at about 1100 cm^{-1} is observed in zeolites [9, 10]. Quantitative comparison with the $H_8(SiO)_4$ molecule which possesses S_4 symmetry and for which $\nu(Si-H) = 2200 \text{ cm}^{-1}$ and $\nu(Si-O) = 1114 \text{ cm}^{-1}$ have been reported [16] would be very interesting. The i.r. and the Raman active $\nu(Si-H)$ and $\delta(Si-H)$ vibrations in SiH_4, Si_6H_{12} and $H_8Si_8O_{12}$ reported in Table 9 lead to the conclusion that the force constants of the comparable modes in these molecules are very similar, an observation which is supported when comparing the force constants of these molecules [17, 18]. Thus many of the force constants of a large variety of silicon hydride and silicon oxide compounds seem to vary only little. This will help to simplify quantum chemical force field calculations of such structures.

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