

RAPID COMMUNICATION

Infrared and Raman spectra of octa(hydridosilasesquioxanes)

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Abstract—We report the NIR FT-Raman spectrum of $H_8Si_8O_{12}$ and the fundamental IR modes of $D_8Si_8O_{12}$. The fundamental modes are assigned according to a normal coordinate analysis and in terms of internal vibrations.

INTRODUCTION

We have recently described the normal coordinate analysis of the fundamental vibrations of octa(hydridosilasesquioxane) $H_8Si_8O_{12}$ [1]. The IR spectrum of this molecule was well known at that time but only preliminary information on the Raman spectrum was available. We have now measured it carefully and we have also been able to prepare the isotopically substituted molecule $D_8Si_8O_{12}$ by a Pd-catalysed deuterium exchange [2] and to observe its IR spectrum. Since the electronic structure of $H_8Si_8O_{12}$ is well understood and since we know that the reaction mechanism of the Si-H→Si-D substitution proceeds via a five-coordinate silicon intermediate followed by concerted rearrangement of angles and bond distances [3], it has become even more interesting to get a clear idea on the vibrational structure of this molecule. While the proton and the silicon NMR of octa(hydridosilasesquioxane) in solution consist each of a single line [4], thus indicating ideal octahedral symmetry, careful X-ray analysis shows lowering of the symmetry in the crystalline form from O_h to T_h [5].

In this communication we report the full Raman spectrum of $H_8Si_8O_{12}$ and the fundamental IR modes of $D_8Si_8O_{12}$ and give assignment of the fundamental modes according to our normal coordinate analysis [1] and in terms of the internal vibrations $\nu(\text{Si-H})$, $\nu(\text{Si-O})$, $\delta(\text{O-Si-H})$, $\delta(\text{O-Si-O})$ and $\delta(\text{Si-O-Si})$. We use the same symbols as explained in [1]. Justification of our assignment and symmetry force constants as well as internal force constants will be given in a forthcoming paper where the harmonic force field of $H_8Si_8O_{12}$ will be critically explored [6].

EXPERIMENTAL

The FTIR spectra were recorded on a BOMEM DA3.01 FTIR spectrometer. The $H_8Si_8O_{12}$ spectra were measured in the range 4000–400 cm^{-1} with a CuGe detector using a KBr beamsplitter, and in the range 700–200 cm^{-1} with a DTGS detector using a 6 μm Mylar beamsplitter. The $D_8Si_8O_{12}$ spectra were recorded with a MCT detector using a KBr beamsplitter in the range 4000–700 cm^{-1} , and in the range 700–200 cm^{-1} with a DTGS detector using a 6 μm Mylar beamsplitter. $H_8Si_8O_{12}$ as well as $D_8Si_8O_{12}$ were solved in CCl_4 and measured in a 0.2 mm CsI cell.

The NIR FT-Raman spectra were measured on the same instrument. A Quantronix 114 cw Nd:YAG laser was used as excitation source operating in single TEM_{00} mode at 9394.5 cm^{-1} . The laser beam was focused on the probe to increase the spectral intensity. Collection of the Raman signal was made with a backscattering geometry including an ellipsoidal mirror. To obtain spectra with a good signal-to-noise ratio it is essential to reduce the intensity of the Rayleigh line which was

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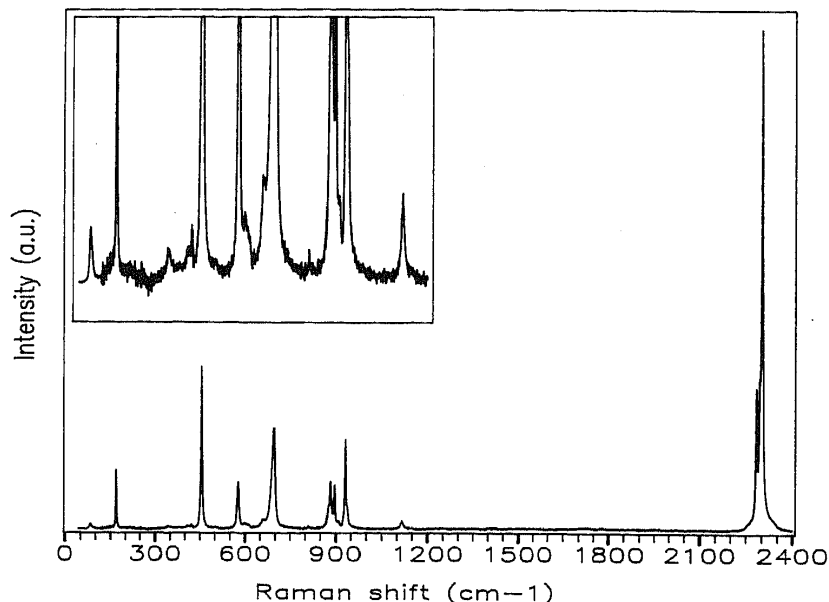


Fig. 1. Raman spectrum of $\text{H}_8\text{Si}_8\text{O}_{12}$ powder.

guaranteed by a set of notch filters. Raman scattering was measured with a liquid nitrogen cooled InGaAs detector of a NEP of $9.2 \times 10^{-15} \text{ W/Hz}^{1/2}$. A quartz beamsplitter was used.

The Raman spectrum was recorded from powdery $\text{H}_8\text{Si}_8\text{O}_{12}$ with a resolution of 1 cm^{-1} . To prevent losses of Raman intensity and to inhibit effects by glass walls the powder was slightly pressed into a hole in a thin sheet of Pyrex glass. The hole had a diameter of 2 mm. This technique has the advantage that the laser beam can be directly focused on the probe and that the laser power can easily be controlled. The laser power used was 0.9 W.

When recording the Raman spectrum of $\text{H}_8\text{Si}_8\text{O}_{12}$ the main difficulties are that this molecule is only a weak Raman scatterer and that it decomposes if the energy density of the excitation source at the focus becomes too high. Moreover, attention has to be paid to the possibility that intrinsic fluorescence or fluorescence caused by small amounts of impurities may obscure the Raman signal. Although several methods have been developed to circumvent the fluorescence problem, a very practical one is to lower the excitation frequency below the threshold of any fluorescence processes and at the same time to prevent any photochemically induced decomposition. The idea of excitation in the NIR has been known for a long time, but problems in filter and detector technology have delayed a breakthrough for many years. In 1986, HIRSCHFELD and CHASE [7] demonstrated the feasibility of Fourier transform Raman spectroscopy using a NIR laser. Thus, it has now become possible to record NIR FT-Raman spectra of quite sensitive probes, as demonstrated in Fig. 1.

RESULTS AND DISCUSSION

The observed IR active fundamental modes of the two isotopic molecules are shown in Table 1. Because of its low intensity, the fundamental mode ν_{28} of $\text{D}_8\text{Si}_8\text{O}_{12}$ could not be

Table 1. Observed IR active fundamental modes

Normal mode	$\text{H}_8\text{Si}_8\text{O}_{12}$ (cm^{-1})	$\text{D}_8\text{Si}_8\text{O}_{12}$ (cm^{-1})	Type of vibration	
			$\text{H}_8\text{Si}_8\text{O}_{12}$	$\text{D}_8\text{Si}_8\text{O}_{12}$
T_{1u}				
ν_{24}	2276	1658	$\nu(\text{Si-H})$	$\nu(\text{Si-D})$
ν_{25}	1140	1139	$\nu(\text{Si-O})$	$\nu(\text{Si-O})$
ν_{26}	881	687	$\delta(\text{O-Si-H})$	$\delta(\text{O-Si-D})$
ν_{27}	566	531	$\delta(\text{O-Si-O})$	$\delta(\text{O-Si-O})$
ν_{28}	465	*	$\nu(\text{Si-O})$	
ν_{29}	399	391	$\delta(\text{O-Si-O})$	$\delta(\text{O-Si-O})$

* See text.

Table 2. Observed Raman active fundamental modes

Normal mode	$\text{H}_8\text{Si}_8\text{O}_{12}$ (cm^{-1})	Type of vibration
A_{1g}		
ν_1	2302	$\nu(\text{Si-H})$
ν_2	579	$\delta(\text{O-Si-H})$
ν_3	456	$\nu(\text{Si-O})$
E_g		
ν_5	932	$\delta(\text{O-Si-H})$
ν_6	697	$\nu(\text{Si-O})$
ν_7	345	$\delta(\text{O-Si-O})$
ν_8	84	$\delta(\text{Si-O-Si})$
T_{2g}		
ν_{12}	2286	$\nu(\text{Si-H})$
ν_{13}	1118	$\nu(\text{Si-O})$
ν_{14}	897, 883	$\delta(\text{O-Si-H})$
ν_{15}	609	$\nu(\text{Si-O})$
ν_{16}	411	$\delta(\text{O-Si-O})$
ν_{17}	171	$\delta(\text{O-Si-O})$

observed precisely but its value is about 450 cm^{-1} and the type is $\nu(\text{Si-O})$. The assignments of the types of vibration are based on the PED analysis according to [8].

Figure 1 shows the Raman spectrum of $\text{H}_8\text{Si}_8\text{O}_{12}$ powder. It is not corrected for its intensity response function. The two sharp lines at 423 and 811 cm^{-1} , easily observed in the inset, do not represent $\text{H}_8\text{Si}_8\text{O}_{12}$ vibrations. They are probably due to folding of laser lines. The experimentally observed Raman active fundamental modes are collected in Table 2. In order to assure correct assignment of the symmetry species to the fundamental modes, polarized measurements were carried out on suspensions of $\text{H}_8\text{Si}_8\text{O}_{12}$ in CCl_4 and in cyclohexane. From these measurements it has been possible to assign the totally symmetric vibrations. The assignment of the remaining fundamental modes to the symmetry species E_g and T_{2g} was performed as described in Ref. [1]. From this analysis we expect two Raman active fundamentals in the region $800\text{--}1000\text{ cm}^{-1}$, an E_g and a T_{2g} type. Three bands are observed, however. Based on the symmetry lowering in the crystal, it makes sense to attribute the 883 and 897 cm^{-1} bands to a splitting of the T_{2g} vibration.

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