

VIBRATIONAL SPECTRA AND CALCULATION OF THE NORMAL VIBRATIONS

OF 1,3-DIMETHYL-1,1,3,3-TETRACHLORODISILOXANE

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The vibrational spectra of 1,3-dimethyl-1,1,3,3-tetrachlorodisiloxane (DMTChDS) were obtained in [1] where the $\nu(\text{SiO})_g$ and $\nu(\text{SiO})_{as}$ bands were identified. No calculation of the frequencies and forms of the normal vibrations was carried out.

We have recorded the IR spectra of DMTChDS in the gaseous, liquid, and crystalline states and the Raman spectra in the liquid and crystalline states (Fig. 1). The frequencies and forms of the normal vibrations of this molecule have been calculated in order to provide a more reliable interpretation of the vibrational spectra. On account of the lack of data concerning the geometry of this molecule, data on hexachlorodisiloxane (HChDS) and hexamethyldisiloxane (HMDS) from [2, 3] were employed. The following parameters were used: R_{SiO} 1.60 Å, R_{SiC} 1.88 Å, R_{SiCl} 2.01 Å, R_{CH} 1.09 Å, SiOSi 146°. The angles at the Si atoms were assumed to be tetrahedral. Retarded internal rotation around the Si-O bonds is possible in DMTChDS as a result of which this molecule can exist in the form of several conformers of C_1 , C_s , C_2 , and C_{2v} symmetry. In carrying out the calculations it was assumed that one of the SiCl or SiC bonds of the $\text{CH}_2\text{Cl}_2\text{Si}$ - groups lies on the SiOSi plane in a trans-position with respect to the SiO bond (Fig. 2) although in [2] it was concluded that there is some deviation from the planar structure of the trans-chain in HChDS. We carried out calculations for all four conformers using the one and the same force constant matrix which was set up using data on the force fields obtained in [4] for HChDS and HMDS. No additional refinement of the force field was carried out. The results of the calculations are shown in Table 1. The calculation enabled one to assign the experimental frequencies using the calculated forms of the vibrations. There is no doubt concerning the assignment of the frequencies of 2990 and 2918 cm^{-1} to the $\nu(\text{CH})_{as}$ and $\nu(\text{CH})_g$ valence vibrations respectively and the frequencies of 1405 and 1270 cm^{-1} to the $\delta(\text{CH}_3)_{as}$ and $\delta(\text{CH}_3)_g$ deformation vibrations. The absorption bands in the 760-850 cm^{-1} region are assigned to $\rho(\text{CH}_3)$ and, moreover, the vibration with a frequency at around 800 cm^{-1} is very strongly mixed with $\nu(\text{SiO})_g$. The antisymmetric $\nu(\text{SiO})_{as}$ vibration appears in the spectrum as a strong broad band the position of which varies somewhat upon passing from the liquid to the crystal (1095 cm^{-1} in the liquid and 1145 cm^{-1} in the crystal) which may be associated with an increase in the SiOSi angle in the crystal in comparison with this angle in the liquid [5-7]. Two frequencies, 680 and 645 cm^{-1} , may be assigned to the $\nu(\text{SiO})_g$ vibration. The first only appears in the IR spectrum as a very weak band which is most probably a combination frequency or an overtone and it is therefore more reasonable to assign the weak band at 645 cm^{-1} in the IR and Raman spectra to $\nu(\text{SiO})_g$. It is partially polarized in the Raman spectrum. The weak, depolarized band in the Raman spectrum at 755 cm^{-1} is assigned to the $\nu(\text{SiC})$ valence vibration. The assignment of the valence vibrations of the SiCl_2 groups, the vibrational frequencies of which are shown in Table 1, also does not present any significant difficulty. The assignment of the deformation vibrations of the $\text{CH}_2\text{Cl}_2\text{Si}$ - fragment is considerably more difficult. These vibrations are very strongly mixed with one another and any specific assignments can only be made provisionally (Table 1).

Comparison of the IR and Raman spectra of DMTChDS in the various different states of aggregation shows that significant changes are observed in the region of the skeletal and deformation vibrations of the $\text{CH}_2\text{Cl}_2\text{Si}$ - spinning top.

For instance, the band at 232 cm^{-1} which is strong in the Raman spectrum of the liquid becomes weak in the Raman spectrum of the crystal. The complex band at 340 cm^{-1} with a shoulder on the low-frequency side in the Raman spectrum of the liquid has a symmetric contour with a maximum at 325 cm^{-1} in the spectrum of the crystal. In the IR spectrum of the crystal a doublet is observed at 325 and 319 cm^{-1} instead of the band at 340 cm^{-1} . There is a sig-

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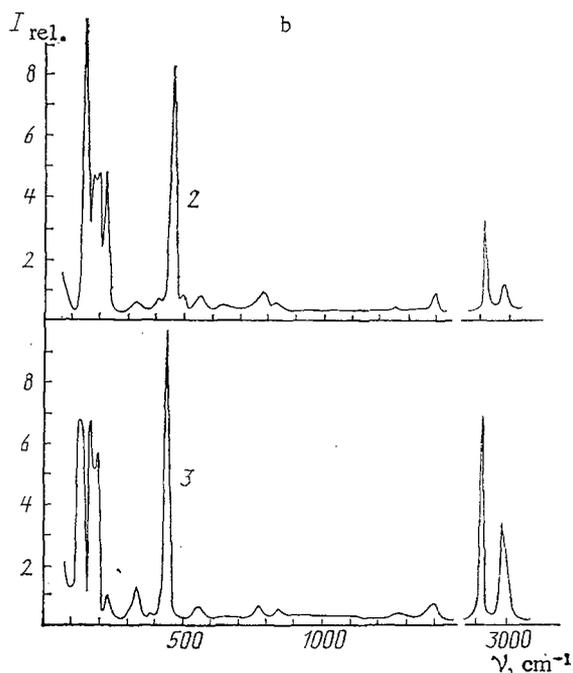
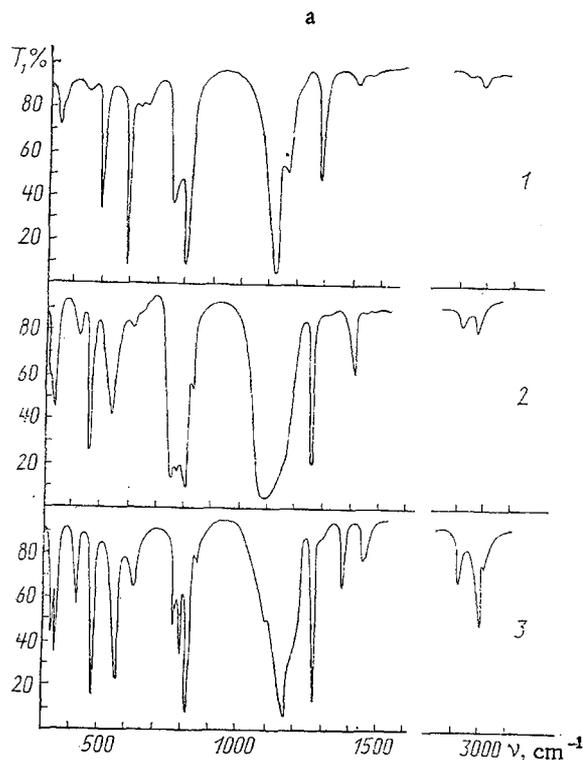


Fig. 1. IR spectra (a) and Raman spectra (b) of DMTChDS: 1) gas, 2) liquid, 3) crystal.

nificant decrease in the intensity of the line at 145 cm^{-1} and the bands associated with the $\nu(\text{SiCl}_2)$ vibrations are shifted to lower frequencies in the spectrum of the crystal as compared with that of the liquid. All these changes, including the shift of the band due to the $\nu(\text{SiO})_{\text{as}}$ valence vibration can hardly be explained unless there is an increase in the SiOSi angle. Apparently, the changes indicated above are associated with a change in the conformational structure.

Apart from the investigation of the vibrational spectra in the various different phase states, we also studied the temperature dependence of the spectra within the limits of a single phase. The investigation were carried out over the following temperature ranges:

TABLE I. Calculated and Experimental Values of the Vibrational Frequencies of the $(\text{CH}_3\text{Cl}_2\text{Si})_2\text{O}$ Molecule

| Experiment | | | | Calculation | | Provisional assignment |
|------------|---------|---------|--|-------------|--------|----------------------------|
| Raman | IR | No. | conformer, frequency (cm^{-1})* | | | |
| Liquid | gas | crystal | liquid | crystal | | |
| 2985 m, dp | 2990 w | 2982 m | 2990 w | 2980 m | 1-4 | $\nu(\text{CH})_{as}$ |
| 2918 s, p | 2915 w | 2912 s | 2918 w | 2915 w | 5,6 | $\nu(\text{CH})_s$ |
| 1406 w, dp | 1440 vw | 1401 w | 1450 vw | 1445 w | 7-10 | $\delta(\text{CH}_3)_{as}$ |
| 1270 vw, p | 1410 vw | | 1405 w | 1390 w | | |
| | 1275 s | | 1270 s | 1265 vs | 11, 12 | $\delta(\text{CH}_3)_s$ |
| | 1195 vw | | | | | Combination |
| 835 w | 1110 vs | 832 w | 1095 vs | 1145 vs | 13 | $\nu(\text{SiO})_{as}$ |
| | 820 sh | | 835 sh | 828 w | 14 | $\rho(\text{CH}_3)$ |
| 773 w, pp | 800 s | 771 w | 800 vs | 790 vs | 15 | $\rho(\text{CH}_3)$ |
| | 760 sh | | 775 w | 768 m | 16 | $\rho(\text{CH}_3)$ |
| 756 vw, dp | 750 m | | 754 vw | 760 sh | 17 | $\rho(\text{CH}_3)$ |
| | 682 vw | | 680 vw | 752 m | 18 | $\nu(\text{SiC})$ |
| 644 vw, dp | 645 vw | | 645 vw | 682 vw | 19 | $\nu(\text{SiC})$ |
| | 615 vw | | 645 vw | 645 vw | 20 | $\nu(\text{SiO})_s$ |
| 562 w, dp | 580 s | 625 vw | 570 s | 625 w | 21 | $\nu(\text{SiCl}_2)_{as}$ |
| 489 vw | 490 m | 554 w | 489 m | 555 s | 22 | $\nu(\text{SiCl}_2)_y$ |
| 448 vs, p | 450 w | 430 vs | 445 m, w | 479 s | 23 | $\nu(\text{SiCl}_2)_{as}$ |
| | | | | 425 w | 24 | $\nu(\text{SiCl}_2)_f$ |
| | | | | | | $\nu(\text{SiCl}_2)_s$ |
| 400 vw | | 405 sh | | | 25 | $\delta(\text{ClSiO})$ |
| 340 w, dp | 340 w | 325 | 340 m | 326, 319 ms | 26 | $\delta(\text{ClSiO})$ |
| | | | | | 27 | τCH_3 |
| 232 m, dp | | 238 | | | 28 | $\delta(\text{ClSiO})$ |
| | | | | | 29 | $\rho(\text{SiCl}_2)$ |
| | | | | | 30 | τCH_3 |
| | | | | | 31 | $\delta(\text{ClSiC})$ |
| | | | | | 32 | $\delta(\text{SiCl}_2)$ |
| 196 m, dp | | 200 | | | 33 | $\delta(\text{SiCl}_2)$ |
| 176 m, dp | | 187 | | | 34 | $\rho(\text{SiCl}_2)$ |
| 145 vs, dp | | 144 | | | 35 | $\rho(\text{SiCl}_2)$ |
| | | | | | 36 | $\rho(\text{SiCl}_2)$ |
| | | | | | 37 | $\delta(\text{SiOSi})$ |
| | | | | | 38 | $\tau(\text{SiO})_{as}$ |
| | | | | | 39 | $\tau(\text{SiO})_s$ |

*Frequencies which according to the calculation do not differ by more than $\pm 5 \text{ cm}^{-1}$ for the different conformers at the maximum value of the calculated band energy for the one and the same internal coordinate are given once without indicating the conformer.

†The coordinate with the maximum value of the calculated band energy is indicated.

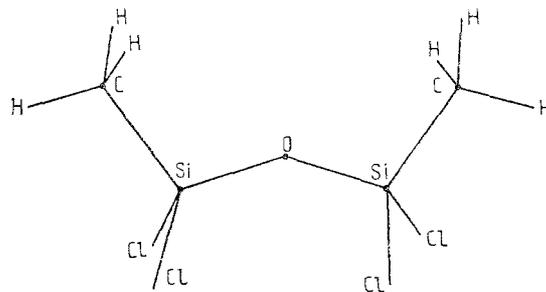


Fig. 2. The DMTChDS conformer with C_{2v} symmetry.

100-20°C in the case of the gas (IR), 20 to -20°C for the liquid, and -25 to -140°C for the crystal (Raman) and down to -190°C (IR). No substantial changes in the spectra were noted during this work.

Deformation vibrations are the most sensitive to rotational isomerism. Calculation showed that this is also observed in the case of the DMTChDS molecule. When this occurs, vibrations which are similar in form may differ in frequency while vibrations of different forms occurring in different conformers may have very similar frequencies. It is therefore impossible to arrive at an unambiguous judgement concerning a change in the conformation structure of DMTChDS from a comparison of the spectra for the various different states of aggregation even if such a change does occur.

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