# *The Infrared Spectra of Methylhydropolysiloxanes*

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Infrared spectra of methylpolysiloxanes were studied by Wright and Hunter[1] and their conclusions were ascertained by Richards and Thompson[2]. There are characteristic absorption bands common to all the methylpolysiloxanes at 1260 cm$^{-1}$ ($CH_3$—Si) and 1000—1100 cm$^{-1}$ (Si—O—Si), and the characteristic bands associated with the structural units were found as follows;

| Unit | Absorption Band (cm$^{-1}$) |
|---|---|
| $(CH_3)_3SiO_{1/2}$ | 841, 754—6 |
| $(CH_3)_2SiO_{2/2}$ | 800—14 |
| $CH_3SiO_{3/2}$ | 800 |

From these, one can conclude that the assignment of the group frequency to the siloxane unit is satisfactory.

It is interesting to study methylhydropolysiloxanes having hydrogen atoms attached directly to silicon atoms. Recently, methylhydropolysiloxanes[3] involving the units, $H(CH_3)_2SiO_{1/2}$ and $H(CH_3)SiO_{2/2}$, were synthesized. In this paper, the infrared spectra of these compounds will be described and especially it is intended to determine whether the group frequency can be assigned or not to these units.

The following short hand notation will be used to indicate the various polysiloxanes.

| Notation | Unit |
|---|---|
| **M'** | $H(CH_3)_2SiO_{1/2}$ |
| **M** | $(CH_3)_3SiO_{1/2}$ |
| **D'** | $H(CH_3)SiO_{2/2}$ |
| **D** | $(CH_3)_2SiO_{2/2}$ |
| **T** | $CH_3SiO_{3/2}$ |
| **Q** | $SiO_{4/2}$ |

## Experimental

**Materials.**—The compounds used in this experiment were as follows:

Linear polysiloxanes;
$\mathbf{M'D'_nM'}$ $n=0, 1, 2, 3$
$\mathbf{MD'_nM}$ $n=1, 2, 3, 4, 5$
$\mathbf{M'D_nM'}$ $n=1, 2$
**M'D'DM'**, **MM'**

cyclic polysiloxanes;
$\mathbf{D'_n}$ $n=4, 5, 6$
$\mathbf{D'_nD_{4-n}}$ $n=1, 2, 3$

branched polysiloxane;
$\mathbf{M'_3T}$

**Measurements.**—Spectra were obtained with a Hilger H-800 infrared spectrophotometer with a rock salt prism. Samples were observed as solutions, 2∼5% solution in carbon disulfide being used in the range 700 to 1500 cm$^{-1}$ and 3∼5% in carbon tetrachloride from 1250 to 5000 cm$^{-1}$. Pure liquid was also used. No appreciable difference was observed between both cases. The cells were 0.03 mm. thick for solution and less than 0.01 mm. for pure liquid. In order to compare relative intensities approximately, the spectra of the compounds belonging to the same series (such as $\mathbf{M'D'_nM'}$, $n=0-3$) were recorded on a same chart, keeping the conditions as similar as possible. $\mathbf{M'_2}$, **M'D'M'**, $\mathbf{M'D'_2M'}$, $\mathbf{M'D'_3M'}$ and **M'D'DM'** were measured also with a Perkin-Elmer Model 21 spectrophotometer with a calcium fluoride prism in the range 1500 to 3300 cm$^{-1}$. The cells were 0.026 and 0.109 mm. thick and the concentration of the solution was 3% in carbon tetrachloride. The spectra and the position of the absorption bands are presented in Fig. 1 and Table I∼III respectively.

TABLE I

METHYLHYDROPOLYSILOXANES: POSITIONS OF BANDS (in cm$^{-1}$)

| $\mathbf{D'_n}$ | | | $\mathbf{D'_nD_{4-n}}$ | | |
|---|---|---|---|---|---|
| $n=4$ | 5 | 6 | $\mathbf{D'D_3}$ | $\mathbf{D'_2D_2}$ | $\mathbf{D'_3D}$ |
| 771 | 769 | 767 | 751 | 755 | 761 |
| | | | 801 | 798 | 795 |
| | | | 818 | 826 | 831 |
| 880 | 874 | 870 | | 867 | 858 |
| | 893 | 892 | | | 884 |
| 917 | 916 | 919 | 906 | 905 | 903 |
| 1085 | 1086 | 1082 | 1070 | 1078 | 1081 |
| 1258 | 1258 | 1258 | 1256 | 1256 | 1258 |
| | | | 1397 | 1395 | 1399 |
| 1405 | 1409 | 1409 | 1407 | 1408 | 1410 |
| 2162 | 2159 | 2162 | 2148 | 2158 | 2170 |
| 2991 | 2987 | 2991 | 2990 | 2985 | 2991 |

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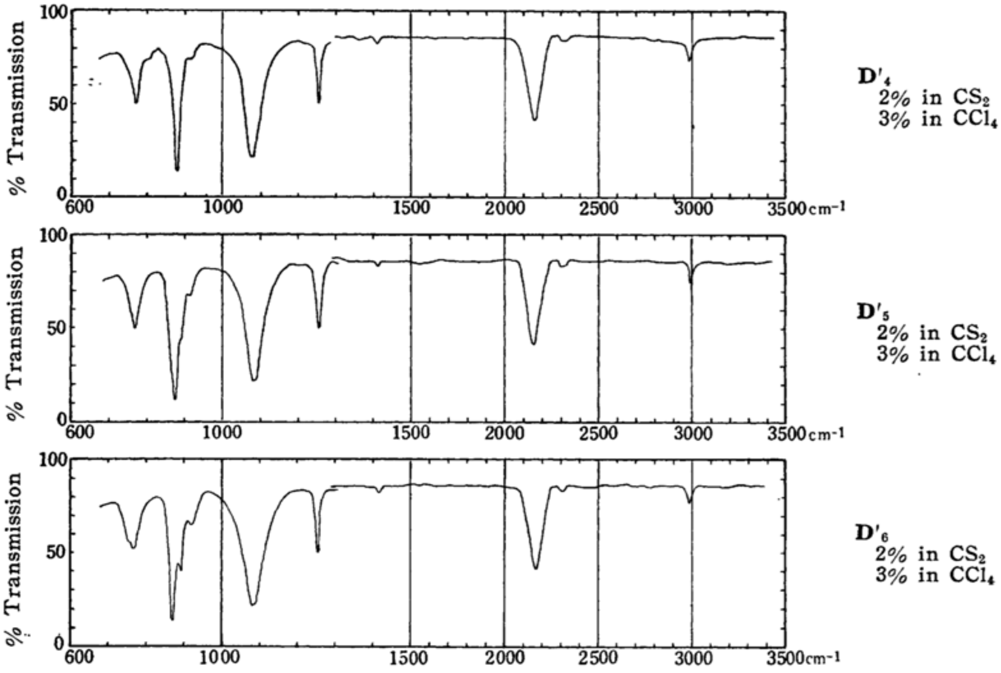
[1] N. Wright and M. J. Hunter, *J. Am. Chem. Soc.*, **69**, 803 (1947).

[2] R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, **1949**, 124.

[3] R. Okawara and M. Sakiyama, This Bulletin, **29**, 236, 547 (1956); R. Okawara, U. Takahashi and M. Sakiyama, ibid., **30**, 608 (1957).

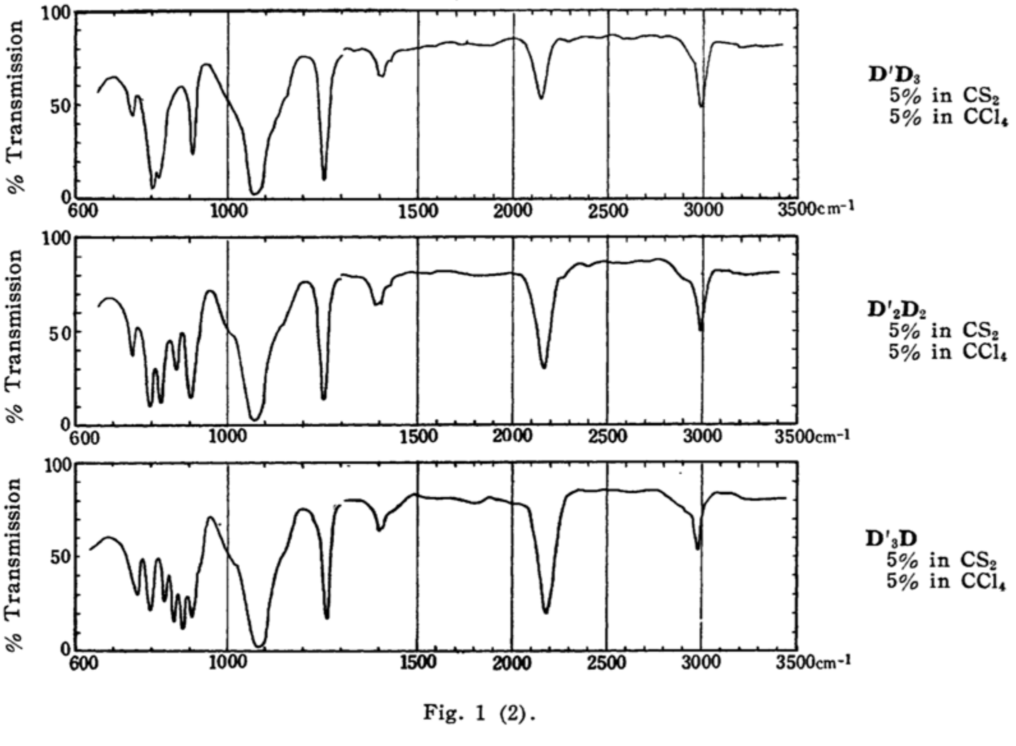


**$D'_4$**
2% in $CS_2$
3% in $CCl_4$

**$D'_5$**
2% in $CS_2$
3% in $CCl_4$

**$D'_6$**
2% in $CS_2$
3% in $CCl_4$

Fig. 1 (1).

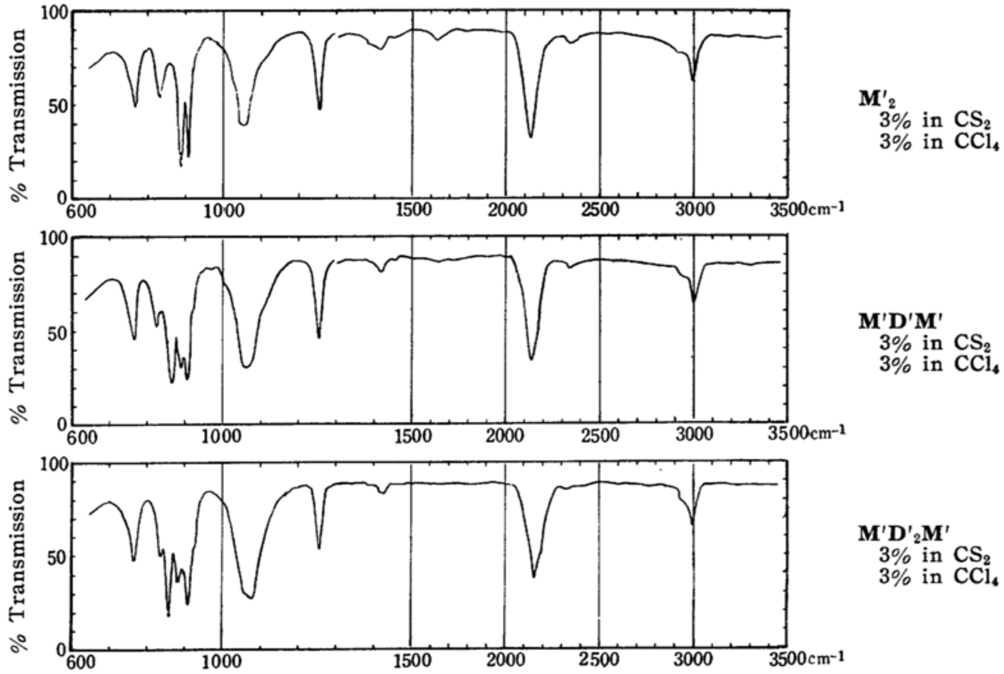


**$D'D_3$**
5% in $CS_2$
5% in $CCl_4$

**$D'_2D_2$**
5% in $CS_2$
5% in $CCl_4$

**$D'_3D$**
5% in $CS_2$
5% in $CCl_4$

Fig. 1 (2).

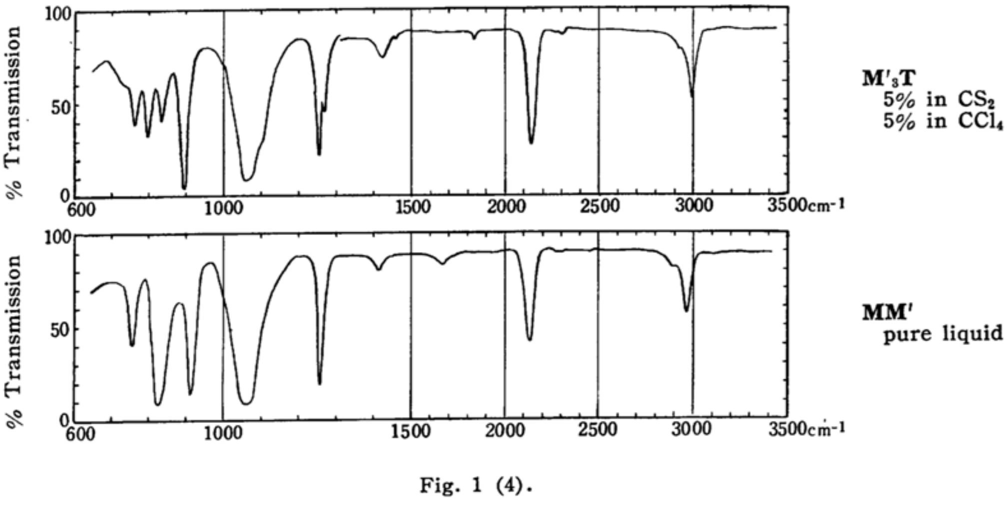


**$M'_2$**
3% in $CS_2$
3% in $CCl_4$

**M'D'M'**
3% in $CS_2$
3% in $CCl_4$

**$M'D'_2M'$**
3% in $CS_2$
3% in $CCl_4$

Fig. 1 (3).



**$M'D'_3M'$**
3% in $CS_2$
3% in $CCl_4$

**$M'_3T$**
5% in $CS_2$
5% in $CCl_4$

**MM'**
pure liquid

Fig. 1 (4).

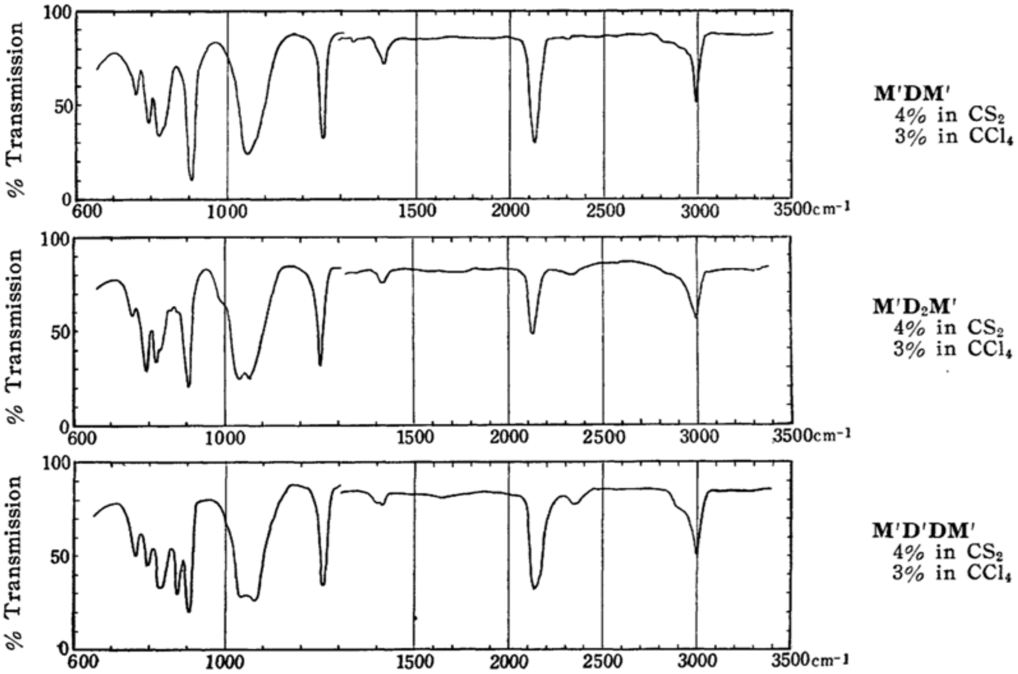

% Transmission
100
50
0
600
1000
1500
2000
2500
3000
3500cm⁻¹
M'DM'
4% in CS₂
3% in CCl₄
M'D₂M'
4% in CS₂
3% in CCl₄
M'D'DM'
4% in CS₂
3% in CCl₄

Fig. 1 (5).

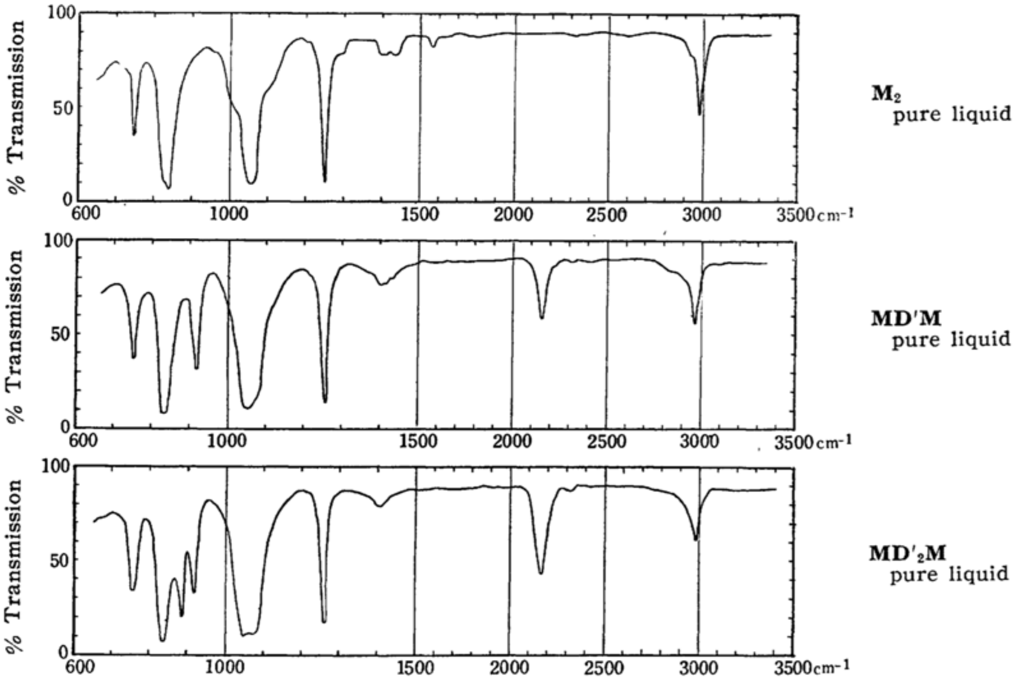

% Transmission
100
50
0
600
1000
1500
2000
2500
3000
3500cm⁻¹
M₂
pure liquid
MD'M
pure liquid
MD'₂M
pure liquid

Fig. 1 (6).

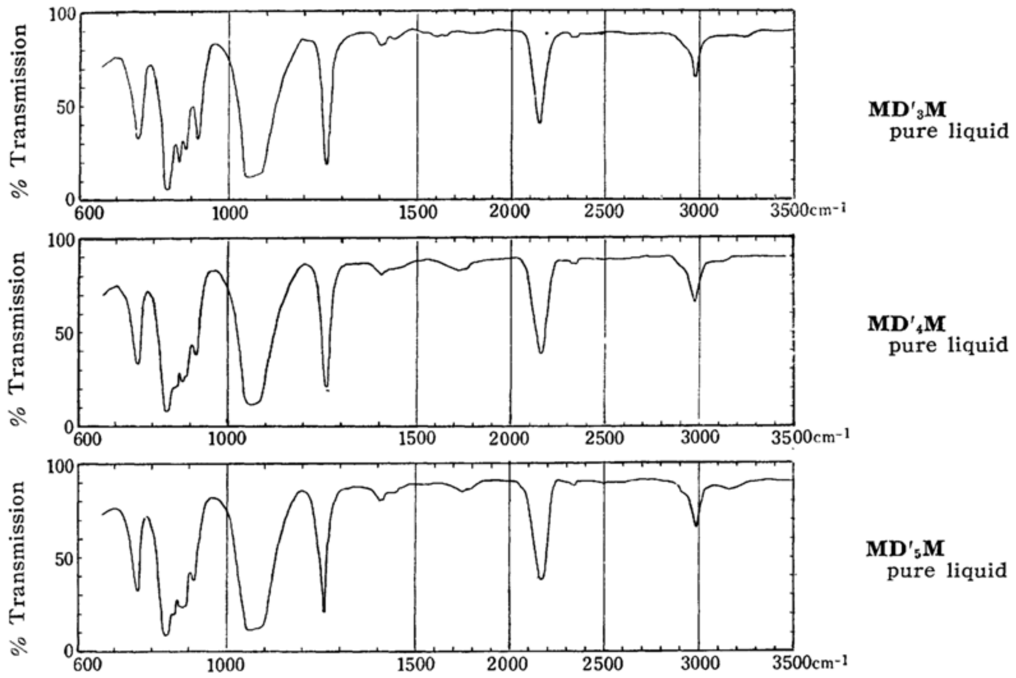


Fig. 1 (7). The infrared spectra of methylhydropolysiloxanes.

TABLE II

METHYLHYDROPOLYSILOXANES: POSITIONS OF BANDS (in $cm^{-1}$)

| M'D'$_n$M' | | | | | | M'D$_n$M' | | |
|---|---|---|---|---|---|---|---|---|
| $n$=0 | 1 | 2 | 3 | **MM'** | **M'$_3$T** | **M'DM'** | **M'D$_2$M'** | **M'D'DM'** |
| 763 | 764 | 763 | 765 | 755 | 763 | 760 | 759 | 761 |
| | | | | | | 794 | 792 | 791 |
| | | | | | 798 | | | |
| 832 | 824 | 833 | 834 | 834 | 830 | 820 | 820 | 826 |
| | 861 | 856 | 854 | | | | | 874 |
| 878 | 885 | 881 | 884 | | | | | |
| 906 | 902 | 905 | 907 | 904 | 899 | 906 | 901 | 904 |
| 1055 | 1063 | 1072 | 1074 | 1054 | 1059 | 1055 | 1037 | 1045 |
| | | | | | | | 1070 | 1075 |
| 1252 | 1255 | 1253 | 1254 | 1258 | 1253 | 1254 | 1254 | 1256 |
| | | | | | 1262 | | | |
| 1416 | 1413 | 1413 | 1413 | 1414 | 1419 | 1412 | 1405 | 1406 |
| 2129 | 2136 | 2137 | 2140 | 2114 | 2132 | 2130 | 2126 | 2134 |
| | 2169 | 2169 | 2169 | | | | | |
| 2931 | 2931 | 2920 | 2922 | 2912 | 2924 | 2920 | 2924 | 2905 |
| 2990 | 2993 | 2988 | 2988 | 2968 | 3004 | 2983 | 2983 | 2983 |

## Discussion of the Results

**Si—H Vibration.**—The most remarkable difference between the spectra of dimethylpolysiloxanes[1,2] and those discussed in this study, is that a strong band in the 2100 $cm^{-1}$ region is present only in the latter. This band is characteristic of the organosilicon compounds containing an Si—H bond, and has been assigned to the stretching vibration involving an Si—H bond[4]. In this case also, it will be attributable to that vibration because all the compounds contain this bond.

Two kinds of methylhydrosiloxy unit, one chain-forming **D'** unit and the other chain-terminating unit **M'**, are involved in the compounds studied. It is of interest to study whether the position of this band

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[4] For example, (a): 2135 $cm^{-1}$ in $(C_6H_5)_3SiH$ and 2108 $cm^{-1}$ in $(n\text{-}C_3H_7)_3SiH$ (L. Kaplan, *J. Am. Chem. Soc.*, **76**, 5880 (1954)) and (b): 2258 $cm^{-1}$ in $HSiCl_3$ (J. G. Gibian and D. S. McKinney, ibid., **73**, 1431 (1951)).

TABLE III

METHYLHYDROPOLYSILOXANES: POSITIONS OF BANDS (in $\mathrm{cm}^{-1}$)

| $\mathbf{MD'_nM}$ | | | | | |
|---|---|---|---|---|---|
| $n$=0* | 1 | 2 | 3 | 4 | 5 |
| 749 | 751 | 762 | 762 | 762 | 762 |
| 826 | 834 | 834 | 834 | 834 | 834 |
| 840 | | | 867 | 860 | 858 |
| | | 879 | 886 | 878 | 875 |
| | | | | 890 | 891 |
| | 914 | 913 | 913 | 912 | 912 |
| 1055 | 1052 | 1046 | 1046 | 1050 | 1052 |
| 1252 | 1258 | 1258 | 1258 | 1258 | 1258 |
| 1405 | 1404 | 1402 | 1405 | 1407 | 1407 |
| | 2149 | 2154 | 2159 | 2159 | 2159 |
| 2927 | 2915 | 2914 | 2918 | 2918 | 2918 |
| 2978 | 2965 | 2978 | 2978 | 2978 | 2978 |

* This spectrum was measured for comparison.

varies in these two units. In $\mathbf{M'_2}$ and $\mathbf{D'_4}$, involving only one kind of unit, this band is found at 2129 $\mathrm{cm}^{-1}$ in the former and 2162 $\mathrm{cm}^{-1}$ in the latter. But in the compounds having both units, this band is not likely to have two peaks. For example, the relation of the bands of $\mathbf{M'D'M'}$ and $\mathbf{M'D'_3M'}$ with that of $\mathbf{M'_2}$ is illustrated in Fig. 2.

A similar broadening of the band is also observed in $\mathbf{M'D'_2M'}$, and $\mathbf{M'D'DM'}$. This band was not separated into two peaks although the spectra were abtained with a spectrophotometer with a calcium fluoride prism. The position of this band shifts to the side of less wave number when the units, **M**, **D** and **T** are introduced in a molecule. This relation is generally seen. For example, in the series $\mathbf{M'D_nM'}$, $\mathbf{D'_nD_{4-n}}$ and $\mathbf{MD'_nM}$, in which Si—H content varies systematically along the series, not only the intensity but also the position of this band changes regularly.

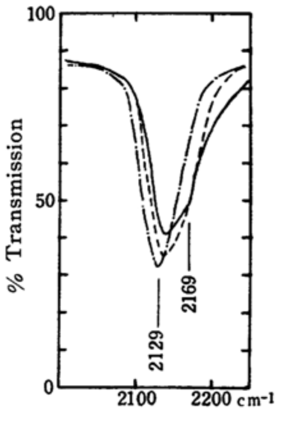

Fig. 2. Si—H stretching vibration bands of $\mathbf{M'D'_nM'}$

—·—·— $\mathbf{M'_2}$ -------- $\mathbf{M'D'M'}$

———— $\mathbf{M'D'_3M'}$

In $\mathbf{M'D'M'}$ and $\mathbf{M'D'_3M'}$, a weak band, which is absent in $\mathbf{M'_2}$ is observed at 2169 $\mathrm{cm}^{-1}$.

Below 1000 $\mathrm{cm}^{-1}$, a common band to all the compounds is observed at 760 $\mathrm{cm}^{-1}$. Of course, **M** may give rise to a band in the same position in $\mathbf{MD'_nM}$ and $\mathbf{MM'}$. This band, though more tentative than in the case of the band described above, seems to be able to be assigned to the bending vibration involving an Si—H bond as was suggested by Ulbrich[5)] with the Raman spectra of $\mathbf{D'_4}$ and $\mathbf{D'_5}$. The position seems to be the same in both **M′** and **D′** units.

This assignment is consistent with the following facts once studied by other authres: (1) Trisubstituted silanes, $HSiCl_3$[4b)] (IR), $HSiBr_3$[6)] (Raman) and $(C_6H_5)_3SiH$[4a)] (IR) give rise to this band at 798, 767 and 805 $\mathrm{cm}^{-1}$ respectively. (2) $H(CH_3)SiCl_2$[5)], which gives $\mathbf{D'_n}$ by hydrolysis, has two bands at 753 and 805 $\mathrm{cm}^{-1}$ in this region, of which only the former is kept in $\mathbf{D_n'}$, while its position attributable to such a vibration will not be expected to vary after hydrolysis. (3) In the series $\mathbf{D_n'D_{4-n}}$ and $\mathbf{M'D_nM'}$, a similar relation is observed for the position and the intensity as was observed in the case of Si—H stretching band when **D′** is replaced by **D**, i.e., both intensity and wave number decrease as $n$ increases.

**C—H Vibration.**—In the region 2900—3000 $\mathrm{cm}^{-1}$, all the compounds show the bands associated with the stretching vibration of C—H linkage. These bands consist of two bands near 2920 and 2980 $\mathrm{cm}^{-1}$. The former is weaker than the latter and may be a combination or overtone band. The latter is also weak as shown in the case of methylpolysiloxane[1)]. It is interesting to compare this intensity with that of Si—H stretching vibration bands.

The band near 1410 $\mathrm{cm}^{-1}$ will be attributed to the methyl deformation vibration. To a sharp intense band near 1260 $\mathrm{cm}^{-1}$ some different assignments have been made. The workers[1)] who studied methylpolysiloxanes attributed them to the methyl rocking vibration and others who studied tetramethylsilane to the sym-

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[5)] R. Ulbrich, *Z. Naturforsch.*, **9B**, 380 (1954).

[6)] J. M. Delfosse and R. G. Ghoovaerts, *Bull. Berg.*, **21**, 410 (1935): F. Francois and H. Buisset, *Compt. rend.*, **230**, 1946 (1950).

metrical deformation mode⁷⁾ or $\gamma$-(CH) vibration⁸⁾ of the methyl group. In this study, it is impossible to determine the assignment of this band, but it has become clearer that this band is related to the $CH_3$-(Si) group since this band is observed in all the compounds. In a branched polysiloxane $\mathbf{M'_3T}$, this band has two peaks at 1253 and 1262 cm$^{-1}$ and the former is more intense than the latter as was reported¹⁾ in $\mathbf{M_3T}$ and $\mathbf{M_4Q}$.

**Si—O Vibration.**—The strong absorption band in the region 1000—1100 cm$^{-1}$ is probably associated with Si—O linkage. This band occurs in the range 1070—1085 cm$^{-1}$ in the cyclic compounds, 1045—1060 cm$^{-1}$ in the linear and the branched compounds. In $\mathbf{M'DM'}$, $\mathbf{M'D'DM'}$ and $\mathbf{M'D_2M'}$, this band consists of two peaks.

**Characteristic Bands below 1000 cm$^{-1}$.** All the bands which have been assigned to **M**, **D** and **T** in the study of methylpolysiloxanes are found without exception also in the spectra of methylhydropolysiloxanes containing these units. In $\mathbf{D'_nD_{4-n}}$, the intensity of 800 cm$^{-1}$ band of **D** clearly increases as is expected from the increasing group concentration, but the wave number is less than those which were reported and decreases as **D** is replaced by **D′**. At least, within the limits of this study, it may be said that the conclusion of Wright and Richards are confirmed.

There are three bands at 906, 878 and 832 cm$^{-1}$ in $\mathbf{M'_2}$. They are observed also in the other members of $\mathbf{M'D'_nM'}$ and their intensities clearly decrease when $n$ increases. In the compounds having both **M′** and other units (**M**, **D** or **T**), i.e., **MM′**, $\mathbf{M'D_nM'}$, $\mathbf{M'D'DM'}$ and $\mathbf{M'_3T}$, only one band is found instead of the former two bands. Therefore it may probably be considered that one or two bands in the range 870—910 cm$^{-1}$ are characteristic of the unit **M′**. The 832 cm$^{-1}$ band is found at the same position also in other compounds but in **MM′** this band may overlap with the **M** band at 841 cm$^{-1}$.

A new band occurs at 861 cm$^{-1}$ in $\mathbf{M'D'M'}$, which is absent in $\mathbf{M'_2}$. This band is caused by the introduction of **D′** unit and moves to the side of lower wave number as the group concentration increases in $\mathbf{M'D_n'M'}$. This band is found at 874 cm$^{-1}$ in $\mathbf{M'D'DM'}$. In $\mathbf{MD'_nM}$, the greater the $n$, the more complex the spectra. All the members of this series ($n \geq 1$) have a band at 914 cm$^{-1}$. Except this band, $\mathbf{MD'_2M}$ has one band, $\mathbf{M'D'_3M}$ has two bands in this region, and so on. The number of bands in this region seems to increase.

A similar complexity is found also in $\mathbf{D'_nD_{4-n}}$. Wright et al.¹⁾ found that $\mathbf{D_4}$ has two bands at 862 (strong) and 880 cm$^{-1}$ (weak). In $\mathbf{D'_nD_{4-n}}$, a common band is found at 900 cm$^{-1}$. Except this band, $\mathbf{D'D_3}$ has a band at 818 cm$^{-1}$, $\mathbf{D'_2D_2}$ has two bands at 827 and 867 cm$^{-1}$ and $\mathbf{D'_3D}$ has three bands at 831, 858 and 884 cm$^{-1}$. On the other hand $\mathbf{D'_4}$ has only one band in this region. It is necessary to point out that $\mathbf{D'_2D_2}$ may be a mixture of two isomers, $\underline{|{-}\mathbf{DDD'D'}{-}|}$ and $\underline{|{-}\mathbf{DD'DD'}{-}|}$. In spite of this, the complexity of the spectra of the compound containing **D′** unit, either linear or cyclic, shows that this unit is less independent than other units and the group frequency treatment must be disclaimed with this unit.

## Summary

1) Infrared spectra of some methylhydropolysiloxanes involving the units, $H(CH_3)_2SiO_{1/2}$ and $H(CH_3)SiO_{2/2}$, were studied. The assignments of Wright and Richards with methylpolysiloxanes were comfirmed in this study.

2) The stretching and the bending band involving an Si—H bond are found in the range 2120—2170 cm$^{-1}$ and 760 cm$^{-1}$, respectively.

3) Characteristic absorption bands of the unit $H(CH_3)_2SiO_{1/2}$ are observed near 900 cm$^{-1}$ and 830 cm$^{-1}$, while the unit $H(CH_3)SiO_{2/2}$ does not give the characteristic band and the band related with this unit is different in each compound.

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7) C. W. Young, J. S. Koehler and D. S. McKinney, *J. Am. Chem. Soc.*, **69**, 1910 (1947).

8) D. H. Rank, B. D. Saksena and E. R. Shull, *Discuss. Farad. Soc.*, **9**, 187 (1950).