# $\nu$(C—F) IN SOME ORGANOSILICON COMPOUNDS*

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IR absorption spectra of compounds of the type $(CH_3)_3MCH_2F$ (M = C, Si), $(CH_3)_3MCH_2Cl$ (M = C, Si, Ge, Sn), $(CH_3)_3SiCH_2X$ (X = Br, I), $(CH_3)_3Si(CH_2)_2Cl$, $Cl_3Si(CH_2)_2X$ (X = = F, Cl) and $(CH_3)_3Si(CH_2)_3X$ (X = F, Cl) have been measured and interpreted. Solvent effects on $\nu$(C—F) around 1 000 $cm^{-1}$ have been investigated.

In continuing the study[1,2] of spectral properties and behaviour[3,4] of α-functional derivatives of the type $(CH_3)_3MCH_2X$ (M = Group IV element, X = halogen), in the present work we tried to interpret some changes in the IR spectra of organometallic derivatives due to the effect of the central atom M and halogen X. We were particularly concerned with the still less known localization of the fundamental stretching frequency of the C—F bond.

## EXPERIMENTAL

Except readily available compounds, the preparation of the others was reported elsewhere[1,2,5-8]. The purity of all the substances was checked by GLC and NMR spectroscopy.

IR spectra were measured on a double-beam prismatic Zeiss (Jena), Model UR 20, spectrometer in the 4000–400 $cm^{-1}$ region. Concentration of solutions of measured compounds in spectroscopically pure $CCl_4$ or $CS_2$ was approx. 7% (by weight). KBr cells were 0·01 cm thick. Frequency scale was calibrated by polystyrene bands.

$(CH_3)_3SiCH_2F$ was also measured in the gas phase, using a gas NaCl cell (10 cm thick), further as the liquid film between KBr plates and as the solution in n-heptane, tetrahydrofuran, deuteriochloroform and acetonitrile. In these solvents the following compounds were also measured: $(CH_3)_3SiCH_2Cl$, $Cl_3Si(CH_2)_2F$, $Cl_3Si(CH_2)_2Cl$, neopentyl fluoride and neopentyl chloride.

## RESULTS AND DISCUSSION

Molecules of model compounds of the type $R_3MCH_2X$ ($R = CH_3$) belong to the $C_1$ or $C_s$ point symmetry group. For $R_3M$ grouping one can also consider the local $C_{3v}$ point symmetry. Molecules of $R_3MCH_2X$ can be approximated by a system

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of 8 mass points to which they belong 18 proper vibration steps of freedom. This rough approximation allows to estimate under given conditions the number of IR active frequencies (18).

The values of wavenumbers of the absorption bands observed in IR spectra of compounds of the series $(CH_3)_3SiCH_2X$ where X is a halogen, along with the approximate intensities of these bands are presented in Table I. On the basis of comparative analysis of the IR spectra of this series and the series of chloromethyl derivatives of Group IV elements, $(CH_3)_3MCH_2Cl$, where M = C, Si, Ge and Sn (Fig. 1) and with the use of literature data[5,9], we succeded in assignment of majority of absorption bands.

Table I shows the effect of the mass and electronegativity of halogen X on the wavenumbers of absorption bands for the series of trimethyl(halogenomethyl)silanes; a marked shift to lower wavenumbers in going from the fluoro to the iodo derivative exists for deformation vibrations of the methylene group adjacent to the halogen in the $1200-1000\ cm^{-1}$ region and also for deformation vibrations of the skeleton in the region below $600\ cm^{-1}$. A small wavenumber decrease within $20\ cm^{-1}$ which is observed for $\varrho(SiCH_3)$ and $\nu(SiC_3)$ vibrations speaks for a significantly restricted transmission of interactions from the terminal halogenomethyl group caused by the silicon atom. Distinct changes can be expected in the case of $\nu$(C—X) stretching vibrations. From the literature[11,12] it becomes evident that these vibrations are of particular interest. Their wavenumbers are sensitive to the bonding and spatial arrangement of the neighbouring substituents in the molecule. This fact is used with advantage, *e.g.* in conformational studies, which were reported[12] especially for the C—Cl bond. On the other hand, for the same reason, these vibrations are little characteristic and sometimes it is not easy to make their unambiguous assignment in the spectra (*cf.* for instance refs[13,14]).

The aim of our work was therefore to assign $\nu$(C—F) stretching frequency in the spectrum of $(CH_3)_3SiCH_2F$ (Table I). This compound is not easy to prepare[1]. To our knowledge, its IR spectrum has not yet been interpreted. In the region around 980 $cm^{-1}$ we observed one, very well isolated and very strong absorption band. We believe that this band can be ascribed to the characteristic stretching vibration of the bond $\nu$(Si)—C—F. This proposal is supported by the finding that the wavenumber of the absorption band maximum, as the only one in the whole spectrum, changes with solvent and with the change in the state of the compound. Table II documents that on increasing solvent polarity, the wavenumber of this band decreases from $987\ cm^{-1}$ (n-heptane) to $970\ cm^{-1}$ (acetonitrile), while the other frequencies vary within $5\ cm^{-1}$ at maximum. The values of $\nu$(C—F) in trimethyl(fluoromethyl)silane measured in the gas and the liquid phase differ by $18\ cm^{-1}$ from one another.

From the spectra of the chloro derivatives of Group IV elements (Fig. 1) it becomes immediately clear that the region around $1000\ cm^{-1}$ is for all the organometallic chloromethyl derivatives of the α-series measured under the same conditions practical-

TABLE I

Wavenumbers and Intensities[a] of Absorption Bands in IR Spectra of Compounds of the Type $(CH_3)_3SiCH_2X$ (X = F, Cl, Br, I), cm$^{-1}$

| X = F[b] | X = Cl[c] | X = Br | X = I | Tentative assignment |
|---|---|---|---|---|
| 596 vw | 584 vw | 553 w | 512 w | $\delta$ skelet. |
| 670 w | 645 s[d] | 617 m | 608 w | $\nu^s$ $SiC_3$ |
| | | 645 vw | 633 vw | |
| 706 m | 703 m | 697 m | 694 s | $\nu^{as}$ $SiC_3$ |
| | | | 700 s[e] | |
| | 745 w[e] | | | |
| 762 m | 760 m | 755 m | 753 m | $\varrho^s$ $SiCH_3$ |
| 792 vw | 788 w | 782 m | 776 s | |
| 848 vs[e] | 850 vs[f] | 850 vs | 843 vs | $\varrho^{as}$ $CH_3$ |
| 858 vs | 860 vs[e] | 860 vs | 856 vs | |
| 982 s | | | | $\nu$ C—F |
| 1 017 vw[e] | | | | |
| 1 119 vw | 1 109 w | 1 052 w | 1 008 w | $\delta$ $CH_2$ |
| 1 218 w | 1 181 m | 1 130 m | 1 079 m | |
| | | | 1 162 w | |
| | | | 1 218 w | |
| 1 251 s | 1 249 vs | 1 251 vs | 1 251 vs | $\delta^s$ $CH_3$ |
| 1 263 m[e] | 1 258 s[e] | 1 260 s[e] | 1 259 s[e] | |
| 1 293 w | 1 276 w[e] | | | |
| | 1 336 vw | 1 309 vw | 1 301 w | $\delta^{scis.}$ $CH_3$, $CH_2$ |
| 1 418 m | 1 391 m | 1 382 m | 1 371 m | |
| 1 470 vw | 1 408 m | 1 411 w | 1 409 m | |
| | | 1 430 vvw | 1 420 w[e] | |
| | | | 1 443 vw | |
| 2 833 w | | | | |
| 2 906 m | 2 902 m | 2 903 w | 2 903 m | $\nu^{as}$ $CH_3$ |
| 2 933 m | 2 926 m | 2 937 m | 2 937 m | $\nu^s$ $CH_2$ |
| 2 963 s | 2 961 vs | 2 961 s | 2 961 s | $\nu^{as}$ $CH_3$, $CH_2$ |

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[a] vs — Very strong; s — strong; *m* — medium; w — weak; vw — very weak. [b] The frequencies observed by us differ somewhat from those reported by American authors[10] (*e.g.* 813 m, 864 vs, triplet 999 vs, 1045 m, 1057 m, 1176 w cm$^{-1}$) who unfortunately did not detail the method used to measure the spectrum. [c] Compare also ref.[9]. [d] Overlap with $\nu$(C—Cl). [e] A shoulder. [f] A broad band.

TABLE II

Solvent Effects on ν(C—F) (in $cm^{-1}$) in $(CH_3)_3SiCH_2F$

| Solvent | ε[a] | ν C—F |
|---|---|---|
| — (gas) | | 998 |
| — (liq.) | | 980 |
| n-Heptane | 1·92 | 987 |
| Tetrachloromethane | 2·23 | 982 |
| Carbon disulphide | 2·64 | 980 |
| Tetrahydrofurane | 7·6 | 978 |
| Deuteriochloroform | [b] | 973 |
| Acetonitrile | 37·5 | 970 |

[a] The values of dielectric constants ε were taken from ref.[15]; ε = 4·8 for $CHCl_3$.

TABLE III

Tentative Assignment of ν(C—F) in Carbofunctional Organosilicon Fluorides and in Neopentyl Fluoride

| Compound | ν C—F, $cm^{-1}$ |
|---|---|
| $(CH_3)_3SiCH_2F$ | 982 |
| $(C_2H_5)_3SiCH_2F$ | 1 005, 980[a] |
| $Cl_3Si(CH_2)_2F$ | 1 048, 1 004 |
| $(CH_3)_3Si(CH_2)_3F$ | 1 057, 1 004 |
| $(CH_3)_3CCH_2F$ | 1 039, 1 010 |

[a] Values of wavenumbers without assignment taken from ref.[16].

TABLE IV

Survey of Reported ν(C—F) (in $cm^{-1}$) for Some Alkyl Halogenides

| Compound (ref.) | X | | | |
|---|---|---|---|---|
| | F | Cl | Br | I |
| $CH_3X_{(12)}$ | 1 049 | 732 | 610 | 533 |
| $(CH_3)_3CX_{(13)}$ | [a] | 580 | 520 | 487 |
| $n$-$C_4H_9X_{(12)}$ | — | 730, 649 | 643, 562 | 584, 500 |
| $CNCH_2X_{(11)}$ | 1051 | 749 | 651 | 589 |

[a] Zeil reports 1205 (ref.[13]), 891 and 751 (ref.[17]), Mann[14] records 1262 $cm^{-1}$ (see text).

ly free of absorption bands. At the same time, the effect of the increasing mass and decreasing electronegativity of the central atom M (in the sequence Si, Ge, Sn) is illustrative. The effect manifests itself in a considerable shift of the wavenumbers of some frequencies: *e.g.* $\nu^{as}(M-C_3)$ 703, 612, 539 'm$^{-1}$; $\nu^{s}(M-C_3)$ 645, 584, 521 cm$^{-1}$; $\varrho^{as}(M-CH_3)$ doublets 850 and 860, 793 and 834, 740 and 778 cm$^{-1}$; $\varrho^{s}(M-CH_3)$ doublets 745 and 760, 680 and 726, 639, and 702 cm$^{-1}$; $\nu^{ns}(CH_3, CH_2)$ 2961, 2980, 2990 cm$^{-1}$.

For the compound $Cl_3Si(CH_2)_2F$ we found five absorption maxima in the 1050 to 950 cm$^{-1}$ region. In harmony with solvent effect and changes in the intensity of absorption bands we assign the frequencies 1006 and 1049 cm$^{-1}$ to the C—F bond (Table III). The remaining three bands (940, 975 and 1036 cm$^{-1}$) relate apparently to the $(CH_2)_2$ grouping. In the spectra of analogous chloro derivative $Cl_3Si(CH_2)_2Cl$ and methyl derivative $(CH_3)_3Si(CH_2)_2Cl$ there are only the bands of this grouping at 893 and 910, 1007 and 1023 cm$^{-1}$.

A similar comparison of the spectra of the $\gamma$-derivatives $(CH_3)_3Si(CH_2)_3X$ (X = F, Cl) (Table III) resulted in finding two very strong absorption bands (1004 and 1057 cm$^{-1}$) in the 1100 – 1000 cm$^{-1}$ region and that only for the fluoro derivative. "Analogous" spectra of $\gamma$-fluoro derivatives and chloro derivatives exhibit other absorption maxima which can be obviously ascribed to vibrations of the $(CH_2)_3$ grouping (*e.g.* for $(CH_3)_3Si(CH_2)_3F$ 1166 and 1193 cm$^{-1}$ and splitting of $\delta^{sciss.}$ at 1400 cm$^{-1}$).

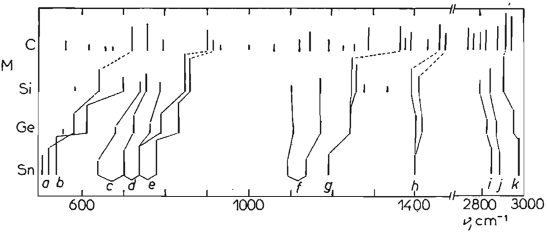

FIG. 1

Diagram of IR Spectra of Compounds of the Type $(CH_3)_3MCH_2Cl$ (M = C, Si, Ge and Sn)

*a* $\nu^{s}MCH_3$, $\nu$(C—Cl); *b* $\nu^{as}MC_3$; *c* $\varrho^{s}MCH_3$; *d* $\varrho CH_2$; *e* $\varrho^{as}MCH_3$; *f* $\gamma CH_2$; *g* $\delta^{s}CH_3$; *h* $\delta^{sciss}CH_3$, $CH_2$; *i* $\nu^{s}CH_3$; *j* $\nu^{s}CH_2$; *k* $\nu^{as}CH_3$, $CH_2$.

As a consequence of "isolating" properties of the heavier and bulkier central atom M, the relatively simple spectra of organometallic compounds make it possible to distinguish the group vibrations of single groupings. This approach has failed, however, in the case of analogous halogeno derivatives of hydrocarbons, because of mutual interactions (coupling). This is manifested in the spectrum by the greater number of absorption bands and by their splitting (Fig. 1). Comparison of the spectra of neopentyl fluoride and neopentyl chloride has shown that the spectra are not at any rate so "similar" as those of silicon analogues. Notwithstanding, the most distinct differences are observed again in the region around 1000 cm$^{-1}$, in which the fluoro derivative shows two significant absorption maxima (Table III). The first band is more intense than the other and its position is more sensitive to solvent effects.

Changes in $\nu$(C—X) of some related compounds (Table IV) are also worthy of mentioning. The greatest difference in $\nu$(C—X) shift is observed when going from F to Cl. Similar differences between other halogenides are not so significant. From Table IV it further follows that the assignment of $\nu$(C—X) frequencies does not have to be always unambiguous. For tert-butyl fluoride, there are several different proposals[13,14,17] as to the $\nu$(C—F) assignment. (Zeil[17] compared experimental data with the values calculated on the basis of potential energy distribution and confirmed that the (C—X) vibration is not "pure" and is coupled with the deformation vibration $\delta \measuredangle$ CCC).

Summarizing the experimental results discussed in the present work, we believe that $\nu$(C—F) frequency in the compounds studied by us is localised in the region around 1000 cm$^{-1}$ (Table III), is solvent-dependent and (*e.g.* Table II) its absorption band is relatively strong. The occurrence of the more than one band can be explained by the existence of conformers.

From Table III it follows that in the $\alpha$-derivative, $\nu$(C—F) is shifted to lower wavenumbers, while in the $\gamma$-derivative it is close to the values reported for carbon compounds.

As to the C—Cl bond, we can state that its frequency is localised in the region of other – for organometallic compounds – very strong absorption bands and cannot be therefore regarded as characteristic (in contradistinction to $\nu$(C—F)) (Fig. 1). Also experiments with different solvents performed with analogous chloro derivatives have not led to positive results.

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