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Abstract

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POTENTIAL FUNCTIONS OF MOLECULES IN THE HOMOLOGOUS SERIES

$(CH_3)_nSiF_{4-n}$ ($n = 1$—4)

(Presented by Academician I. V. Obreimov, 1 VIII 1962)

1. The study of the vibrational properties of methylfluorosilanes is of considerable interest in connection with the development of the chemistry and physics of organosilicon compounds. Up to the present time, experimental data on Raman and infrared spectra have been obtained for molecules of this series, and, incidentally, only individual particular questions of the mechanical vibrational problem have been solved ($^{1-3}$).

2. We have considered the entire series $(CH_3)_nSiF_{4-n}$ ($n = 1$—4). Using the methods of M. V. Vol' kenshtein, M. A. El' yashevich, B. I. Stepanov (^{4}) and L. S. Mayants (^{5}), the coefficients of the potential energy (force constants and interaction coefficients) were calculated, the frequencies and forms of normal vibrations were computed, and, for CH_3SiF_3, the sensitivities of the frequencies to changes in the force constants and the displacements of atoms from equilibrium positions during vibrations were determined. The problem was solved simultaneously for the whole series of methylfluorosilanes, taking into account the results of studies of other halogen-substituted silicon compounds (^{6,7}), as well as SiF_4 (^{8}). The following values for equilibrium bond lengths in the molecules were adopted as the basis (r in Å) (^{9}):

Fig. 1. Equilibrium configuration of the molecule $(CH_3)_3SiF$

	CH_3SiF_3	$(CH_3)_2SiF_2$	$(CH_3)_3SiF$
r(C—H)	1.10	1.09	1.093
r(Si—C)	1.88	1.89	0.87
r(Si—F)	1.555	1.56	1.55

The angles were taken to be tetrahedral. The notation for the coordinate system introduced is given in Fig. 1. In the present work, the interaction coefficients are presented and discussed as those most fully reflecting the form of the potential functions (Table 1).

3. From Table 1 it is seen how the distribution of forces and mutual interactions within the molecules changes in passing from tetramethylsilane to methyltrifluorosilane. Certain regularities are observed. Replacement of methyl groups by fluorine atoms leads to an increase in the strength of the Si—C bond by approximately 10%. A similar effect is also characteristic of analogous chlorine- and bromine-substituted compounds and may be associated with the high electronegativity of the halogens, especially fluorine. Attachment of halogen atoms to silicon causes an inductive effect, i.e., a shift of the electron shell of the molecule toward the halogen. As the number of fluorine atoms attached to silicon increases, the value of the coefficient decreases (within 10–15%)

Table 1

Influence coefficients of methylfluorosilanes (10^6 cm^{-2})

Molecule	1: (Q_1, Q_1)	1: (q', q')	1: (q_1, q_1)	1: $(\alpha_{12}, \alpha_{12})$	1: (β_{12}, β_{12})	1: (β_2, β_2)	1: $k_{2\delta}^{-1}$	1: $(\varepsilon_{12}, \varepsilon_{12})$	1: (γ_1, γ_1)	2: (q_1, q_2)	2: (Q_1, q_1)	2: (q_1, α_{12})	2: (q_1, α_{23})
I CH_3SiF_3	0,205	0,112	0,127	1,228	1,370	–	0,831	–	1,112	−0,003	−0,002	−0,030	0,035
II $(CH_3)_2SiF_2$	0,207	0,124	0,128	1,229	1,287	1,279	0,824	1,118	1,132	−0,003	−0,002	−0,031	0,035
III $(CH_3)_3SiF$	0,209	0,141	0,128	1,227	1,262	1,273	–	1,129	0,930	−0,003	−0,002	−0,031	0,035
IV $(CH_3)_4Si$	0,231	–	0,129	1,226	1,256	–	–	1,123	–	−0,003	−0,002	−0,031	0,034

Molecule	2: (q_1, β_1)	2: (q_1, β_2)	2: (Q_1, β_1)	2: (Q_1, β_2)	2: (Q_1, α_{12})	2: $(\alpha_{12}, \alpha_{13})$	2: $(\alpha_{12}, \beta_{12})$	2: (β_3, β_1)	2: (β_2, α_{12})	2: (β_3, q')	3: (q', Q_1)	3: (q', Q_1)	3: (Q_1, Q_2)
I	−0,040	0,036	−0,055	–	0,055	−0,236	−0,211	−0,308	–	−0,333	−0,009	−0,004	–
II	−0,037	0,035	−0,051	−0,040	0,049	−0,229	−0,220	−0,256	−0,251	−0,333	−0,008	−0,006	0
III	−0,036	0,035	−0,046	−0,039	0,042	−0,226	−0,222	−0,251	−0,244	−0,331	–	−0,006	−0,004
IV	−0,036	0,035	−0,038	–	0,038	−0,221	−0,225	−0,237	–	−0,334	–	–	−0,010

Molecule	3: a_δ^{-1}	3: b_δ^{-1}	3: $[q' (b' \ldots)]$	3: $(\varepsilon_{12}, \gamma) b_\gamma^{-1}$	3: (Q_1, γ_1)	3: (Q_1, γ_2)	3: B_δ^{-1}	3: $[Q Q \varepsilon_{23}]$	3: $d_{\delta\delta}^{-1}$	3: $[\varepsilon_{12}, l_{\gamma\gamma}^{-1} \varepsilon_{13}]$	3: $l_{\gamma\gamma}^{a-1}$	3: $O_{\gamma\delta}^{-1}$	3: $[\gamma (\gamma_1 \gamma_2) \varepsilon_{13}]$
I	−0,040	0,045	−0,071	0,053	−0,030	–	0,030	–	−0,211	−0,172	−0,351	−0,065	–
II	−0,049	[0,063]	−0,057	0,050	−0,049	0,053	0,038	−0,044	–	−0,155	−0,204	[−0,404]	0,228

Molecule	3: a_δ^{-1}	3: $b_\delta^{-1}[q', \varepsilon_{12}]$	3: (b', γ)	3: b_γ^{-1}	3: (Q_1, γ_1)	3: (Q_1, γ_2)	3: $B_\delta^{-1}[Q_1, \varepsilon_{23}]$	3: (Q_1, ε_{23})	3: $l_{\delta\delta}^{-1}[\varepsilon_{12}, \varepsilon_{13}]$	3: $l_{\gamma\gamma}^{-1}$	3: $l_{\gamma\gamma}^{a-1}$	3: $O_{\gamma\delta}^{-1}[\gamma_1, \gamma_2]$	3: $(\gamma_1, \varepsilon_{13})$
III	–	[0,062]	−0,062	–	−0,038	0,038	[0,048]	−0,043	[−0,281]	–	–	[−0,182]	−0,209
IV	–	–	–	–	–	–	[0,042]	−0,042	[−0,249]	–	–	–	–

Table 1 (continued)

Molecule	$O_{\gamma\gamma}^{-1}[\gamma_1, \varepsilon_{23}]$	$O_{\delta\delta}^{-1}$	(Q_1, β_4)	(Q_1, β_5)	(Q_1, β_6)	(Q_1, α_{46})	(Q_1, α_{56})	(q', β_1)	(q', β_2)	(β_1, β_8)	(β_2, β_9)	$\begin{pmatrix}\beta_1, \beta_7\\ \beta_2, \beta_6\end{pmatrix}$	$l_{\alpha\delta}^{-1}(\beta_1, \beta_5)$
I	–	–	–	–	–	–	–	0	0,002	–	–	–	0,012
II	−0,141	−0,206	0	−0,005	–	−0,002	−0,002	0,002	−0,006	0	0,011	0	0,009
III	[−0,150]	–	0,002	0,007	−0,005	−0,002	−0,001	0,004	−0,004	0,004	0,012	0 [0,002]	[−0,005]
IV	–	–	0,008	−0,003	–	−0,002	−0,001	–	–	0,003	0,012	0,001	[−0,006]

Molecule	(γ_1, β_1)	(γ_1, β_2)	(γ_1, β_4)	(γ_1, β_5)	(γ_1, β_8)	$(\varepsilon_{12}, \alpha_{13})$	$(\varepsilon_{12}, \alpha_{23})$	$(\varepsilon_{12}, \alpha_{46})$	$(\varepsilon_{12}, \beta_1)$	$(\varepsilon_{12}, \beta_5)$	$n'^{-1}_{\beta\gamma}[\varepsilon_{12}, \beta_1]$	(q_1, β_2)	(q_2, γ_1)
I	0,033	0,001	–	–	–	–	–	–	–	–	–	−0,001	0,001
II	0,031	0,040	0,010	−0,030	−0,024	–	0,007	0,018	0,039	−0,110	0,004	0,001	0,002
III	0,017	0,027	0,009	−0,023	0,001	0,001	0,004	0,014	0,029	−0,119	[0,071]	0,001	0,001
IV	–	–	–	–	–	–	−0,002	0,011	0,058	−0,123	–	–	–

Molecule	(α_{17}, γ_1)	(q_1, ε_{13})	(q_2, ε_{13})	(α_{13}, γ_1)	(α_{13}, γ_2)	(α_{13}, γ_3)	(α_{23}, γ_3)	$p_{\beta\delta}^{-1}[\varepsilon_{12}, \beta_1]$	$r_{\beta\delta}^{-1}[\varepsilon_{12}, \beta_8]$	(α_{89}, γ_2)	$(\alpha_{13}, \varepsilon_{23})$	(α_{13}, β_9)	(q', α_{13})	(q', α_{23})
I	–	–	–	−0,011	–	–	−0,014	−0,011	−0,013	–	–	*	−0,001	−0,001
II	−0,002	−0,003	0,004	−0,026	0,016	0,016	−0,025	0,012	−0,020	0,013	–	−0,002	0	0
III	0,001	−0,002	0,005	−0,024	0,024	0,003*	−0,023	[−0,030]	[0,011]	0,006	0,002	−0,003	0,001	0,001
IV	–	−0,003	0,006	–	–	–	–	[−0,008]	[0,008]	–	−0,003	−0,001	–	–

Notes. 1. Order of arrangement of the coefficients: 1—diagonal influence coefficients, 2—mutual influences of the coordinates of the Si—CH$_3$ group, 3—groups C(SiF$_n$)C$_{3-n}$ (n = 0-3), 4—interactions of the coordinates of the indicated groups with one another.

2. Brackets denote interactions as applied to the equilibrium scheme of the molecule (CH$_3$)$_3$SiF. Mutual interactions of another type: k_δ^{-1}—(F$_i$SiF$_j$ = δ), a_δ^{-1}—(Si—F$_k$, F$_k$SiF$_j$), b_δ^{-1}—(Si—F$_k$, F$_j$SiF$_m$), b_γ^{-1}—(Si—F$_k$, F$_j$SiC), B_δ^{-1}—(Si—C, FSiF), l_{ij}^{-1} refers to interactions of angles i and j having a common side, O_{ij}^{-1}—of "opposite" angles (having a common vertex), $n'^{-1}_{\beta\gamma}$—(FSiC$_k$, SiC$_k$H) (the angles do not lie in one plane), $p_{\beta\delta}^{-1}$ and $r_{\beta\delta}^{-1}$—(FSiF, SiCH); in the case of $p_{\beta\delta}^{-1}$ the plane SiCH bisects the angle δ.

3. Numbers in square brackets refer to coefficients written in the same brackets.
4. The influence coefficients of SiF_4 are: $(q', q') = 0,100$, $(q'_1, q'_2) = 0,003$, $k_\delta^{-1} = 0,798$, $a_\delta^{-1} = -0,028$, $l_{\delta\delta}^{-1} = -0,200$, $b_\delta^{-1} = 0,028$, $o_{\delta\delta}^{-1} = 0$.

influence $(q', q') = k_{g'}^{-1}$, and consequently the strength of the Si–F bond increases. The influence of the interaction of coordinates in the SiF_j group with one another and with the coordinates of the SiC_k group is manifested.

The values of the coefficients $k^1_{g'}$(Si–Hal) decrease strongly in the direction Br → Cl → F substitution. In contrast to the chloro and bromo derivatives, the accumulation of F atoms has almost no effect on the stiffness of the CSiC angles. The stiffness of the C–H bonds and of the HCH angles changes practically not at all in the molecules of all methylhalosilanes; the stiffness of the HCSi angles decreases somewhat. The mutual influences of coordinates within the methyl group are quantitatively identical for all the compounds considered. The interactions of these coordinates with the remaining ones, corresponding to deformations of other parts of the molecules, differ by no more than 5-10%. The valence ν(C—H) and internal deformation $\delta(CH_3)$ vibrations of types A_1 and A_2 in methylhalosilanes are quite characteristic both in frequency and in form. The same may be said of the symmetric ν(C—H) and $\delta(CH_3)$ vibrations of the methyl group of type E. In rocking vibrations $\rho(CH_3)$, the amplitudes of change of the molecular parameters not belonging to the methyl group differ appreciably. A comparison of the calculated displacements of atoms from their equilibrium positions in normal vibrations in the molecules CH_3SiHal_3 shows that the ν- and δ-vibrations of the CH_3 group are also characteristic in terms of displacements.

The changes in the length of the silicon—carbon bond in vibrations of type A_1 in these molecules are equal (in Å):

	ν(C—H)	$\delta(CH_3)$	ν(Si—C)	ν(Si—Hal)	$\delta(SiHal_3)$
CH_3SiF_3	0.0036	0.0134	0.0395	0.0263	0.0035
$(CH_3)_2SiF_2$	0.0034	0.0139	0.0471	0.0096	0.0009
$(CH_3)_3SiF$	0.0034	0.0139	0.0477	0.0035	0.0022

A particularly sharp difference is characteristic of the valence vibrations ν(Si—Hal).

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Note: Figure translations are in progress. See original paper for figures.