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Abstract

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POTENTIAL FUNCTIONS OF MOLECULES OF THE SERIES

$(CH_3)_nSiCl_{4-n}$ $(n = 1—4)$

(Presented by Academician I. V. Obreimov, 14 IX 1960)

1. Until now, no detailed investigation has been carried out of the potential function of molecules of the methylchlorosilane series. Only attempts have been made to estimate force constants characterizing the strength of individual bonds and angles ($^{1-4}$). In addition, using the approximate Urey—Bradley force-field model, diagonal dynamic coefficients and repulsion coefficients have been calculated for CH_3SiCl_3 (^{5}), $(CH_3)_2SiCl_2$, and $(CH_3)_3SiCl$ (^{6}).

We have studied the entire series of molecules $(CH_3)_nSiCl_{4-n}$. Force constants and interaction coefficients have been calculated, the frequencies and forms of normal vibrations have been computed, and the experimental spectra have been interpreted. In the present work the results of the calculation of the interaction coefficients are given.

2. In solving the problem for methylchlorosilanes, the measured infrared and combination spectra published in (^{7},^{8}), and the results of studies of methylsilanes (^{9},^{10}), were used. The calculation was performed in a natural coordinate system according to the method of M. V. Vol' kenshtein, M. A. El' yashevich, B. I. Stepanov (^{11}), and L. S. Mayants (^{12}), with the entire series of the indicated compounds considered simultaneously. As geometrical parameters (angles—tetrahedral) the following were taken (r in Å):

	r(C—H)	r(Si—C)	r(Si—Cl)
CH_3SiCl_3 (^{5})	1.093	1.876	2.021
$(CH_3)_2SiCl_2$ (^{2})	1.093	1.83	1.99
$(CH_3)_3SiCl$ (^{2})	1.093	1.89	2.09

The coordinate notation is indicated in Fig. 1. The resulting set of interaction coefficients is given in Table 1, where only parameters not equal to zero are recorded.

3. Application of the computed set of constants to the calculation of vibrational spectra showed quite satisfactory agreement between theory and experiment: the calculated frequencies in the main practically coincide with the observed ones.

From comparison of the corresponding diagonal coefficients it is seen that:

1. In passing from tetramethylsilane to methylchlorosilanes, the value of the coefficient (Q_1, Q_1), associated with stretching of Si—C, systematically decreases. The jump is especially significant when one of the methyl groups is replaced by chlorine atoms. The strength of the bond under consideration increases. Analysis of the spectra shows an increase in the frequencies of the corresponding stretching vibrations: for example, for type A_1, from 598 cm^{-1} in $(CH_3)_4Si$ to 764 cm^{-1} in CH_3SiCl_3 (7). This phenomenon apparently occurs as a result of replacement, at the silicon atom, of methyl groups by more electronegative partners, namely chlorine atoms, which leads to strengthening of the covalent character of neighboring bonds (3). L. A. Ignat' eva, P. A. Bazhulin, and I. K. Baeva (13), in agreement with this, point out

Table 1

Influence coefficients of methylchlorosilanes and tetramethylsilane (10^{-6} cm^2)

Molecule	1: (Q_1, Q_1)	1: (q_{10}, q_{10})	1: (q_1, q_1)	1: $(\alpha_{12}, \alpha_{12})$	1: (β_1, β_1)	1: (β_2, β_2)	1: k_δ^{-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_3SiCl_3	0.208	0.231	0.127	1.238	1.343	–	0.801	–	1.027	−0.003	−0.002	−0.031	0.035
II $(CH_3)_2SiCl_2$	0.208	0.247	0.127	1.230	1.310	1.300	0.879	1.247	0.940	−0.003	−0.002	−0.031	0.035
III $(CH_3)_3SiCl$	0.212	0.259	0.128	1.230	1.264	1.277	–	1.169	0.972	−0.003	−0.002	−0.031	0.034
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: (α_{12}, β_1)	2: (β_2, β_3)	2: (β_1, β_2)	2: (α_{12}, β_3)	3: k_δ^{-1}	3: (Q_1, q_{10})	3: (Q_1, Q_2)
I	−0.040	0.036	−0.057	–	0.057	−0.231	−0.219	−0.283	–	−0.338	−0.021	−0.005	–
II	−0.038	0.035	−0.052	−0.045	0.049	−0.228	−0.220	−0.266	−0.260	−0.335	−0.037	−0.006	0.012
III	−0.036	0.035	−0.046	−0.040	0.043	−0.223	−0.224	−0.252	−0.241	−0.334	–	−0.007	0.007
IV	−0.036	0.035	−0.038	–	0.038	−0.221	−0.225	−0.237	–	−0.334	–	–	−0.010

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Molecule	3: a_δ^{-1}	3: b_δ^{-1}	3: $[q_{10}, q_{11}]$ (q, ε_{12})	3: b_γ^{-1}	3: (Q_1, γ_1)	3: β_δ^{-1}	3: $[Q_1, Q_2]$ (Q, ε_{23})	3: (Q_1, ε_{13})	3: $r_{\delta\delta}^{-1}$	3: $[\varepsilon_{12}, \varepsilon_{23}]$ $l_{\gamma\delta}^{-1}$	3: $l_{\gamma\gamma}^{a-1}$	3: $o_{\gamma\delta}^{-1}$	3: $[\gamma_1, \gamma_2]$ $(\gamma, \varepsilon_{13})$ $o_{\varepsilon\varepsilon}^{-1}$
I	−0.027	0.026	−0.042	0.034	−0.035	0.035	–	–	−0.164	0.083	−0.277	0.308	–
II	−0.028	[0.039]	−0.029	0.023	−0.034	0.036	0.039	−0.044	–	−0.214	−0.135	[−0.359]	[0.305]
III	–	[0.041]	−0.041	–	−0.027	[0.035]	0.034	−0.038	[−0.310]	–	–	[−0.212]	[0.299]
IV	–	–	–	–	–	[0.042]	–	−0.042	[−0.249]	–	–	–	−0.128

Table 1 (continued)

Molecule	$o_{\gamma\gamma}^{-1}$	$[\gamma_1, \varepsilon_{23}]$ $o_{\delta\varepsilon}^{-1}$	(Q_1, β_5)	(Q_1, β_4)	(q_{10}, β_1)	(q_{10}, β_2)	(Q_1, β_8)	(β_2, β_9)	(β_1, β_7) (β_2, β_5)	(β_1, β_8)	$l_{\alpha\delta}^{-1}$	$[\beta_1, \beta_5]$	(Q_1, α_{46}), $\alpha_{56})$
I	–	–	–	–	0,001	0,002	–	–	–	–	0,014	–	–
II	0,073	−0,025	0,002	−0,003	0,002	−0,003	–	0,013	0,001	0,002	0,013	0,001	0,001
III	[0,049]	–	0,004	−0,001	0,003	−0,002	−0,006	0,013	[0,002]	0,003	[−0,004]	0,001	0,001
IV	–	–	0,008	−0,004	–	–	–	0,012	0,001	0,003	[−0,006]	−0,002	−0,001

Molecule	(γ_1, β_1)	(γ_1, β_2)	$(\varepsilon_{12}, \beta_5)$	$(\varepsilon_{12}, \beta_1)$	$n_{\beta\gamma}^{-1}$	$[\varepsilon_{12}, \varepsilon_{21}]$	(q_1, β_2)	(q_2, γ_1)	(q_2, ε_{13})	(q_1, ε_{13})	(α_{13}, γ_1)	(γ_1, β_8)	(γ_1, β_5)
I	0,033	0,005	–	–	–	0	0,001	–	–	−0,016	−0,014	–	–
II	0,021	0,036	−0,127	0,042	−0,001	0,001	0,002	0,005	−0,003	−0,019	−0,019	−0,019	−0,027
III	0,011	0,032	−0,126	0,026	[0,074]	0,002	0,001	0,005	−0,002	−0,024	−0,026	−0,022	−0,019
IV	–	–	−0,123	0,058	–	–	–	0,006	−0,003	–	–	–	–

Molecule	(γ_1, β_4)	$(\varepsilon_{12}, \alpha_{46})$	$(\varepsilon_{12}, \alpha_{23})$	(φ_{13}, β_5)	$p_{\beta\delta}^{-1}$	$r_{\beta\delta}^{-1}$	$[\varepsilon_{12}, \varepsilon_{13}]$	(α_{13}, β_8)	(γ_2, α_{89})	(γ_2, α_{89})	$(\varepsilon_{12}, \alpha_{13})$	$(\varepsilon_{23}, \alpha_{13})$	(β_7, α_{13})	(β_9, q_7), $\gamma_1(\alpha_{12}, \gamma_3)$
I	–	–	–	–	−0,011	−0,016	–	–	–	–	–	–	–	–
II	0,031	0,023	0,010	–	−0,007	−0,015	0,006	0,002	–	–	0	−0,003	−0,002	0,007
III	0,025	0,017	0,006	0,003	[−0,025]	[0,016]	0,006	0,006	−0,001	−0,004	0	−0,002	0	0,003
IV	–	0,011	−0,002	–	[−0,008]	[0,008]	–	–	−0,002	−0,003	−0,001	−0,001	–	–

Notes. 1. Order of arrangement of the coefficients: 1 –diagonal; 2 –those referring to interactions of the coordinates of the Si–CH_3 group; 3 –of the group $C(SiCl_n)C_{3-n}$ $(n = 0–3)$; 4 –those referring to interactions of the coordinates of the indicated groups with one another.

2. Brackets denote interactions as applied to the scheme of the molecule $(CH_3)_3SiCl$ (representatives of groups of equivalent coordinates are taken). Coefficients not in brackets denote the mutual influence of the following parameters: k_δ^{-1}–(Cl_jSiCl_j, $j = \delta$), h_δ^{-1}–($SiCl_k$, $SiCl_j$), a_δ^{-1} –($SiCl_k$, Cl_kSiCl_j), b_δ^{-1}–($SiCl_k$, Cl_jSiCl_m), b_γ^{-1}–($SiCl_k$, Cl_jSiC), B_δ^{-1} –(SiC, ClSiCl), l_{ij}^{-1} refer to interactions of angles i and j having a

common side, o_{ij}^{-1}—of "opposite" angles (having a common vertex), $n_{\beta\gamma}^{-1}$—(ClSiC$_r$, SiC$_R$H) (the angles do not lie in one plane; analogy—γ_1 and β_3 in $(CH_3)_2SiH_2$ (11)). $p_{\beta\delta}^{-1}$ and $r_{\beta\delta}^{-1}$—(ClSiCl, SiCH) (in the case of $p_{\beta\delta}^{-1}$ the SiCH plane bisects the angle δ).

3. Numbers in square brackets correspond to coefficients written in the same brackets.

attention to the regular increase in the intensity of the infrared Si—C bands.

2. With accumulation of chlorine atoms at silicon, a small but systematic decrease is also observed in the values of the coefficients corresponding to changes in the C—H bond lengths. The effect considered above is induced in these bonds as well.

Fig. 1. Equilibrium configuration of the molecule $(CH_3)_3SiCl$

Fig. 1. Equilibrium configuration of the molecule $(CH_3)_3SiCl$

3. The interaction of Si—Cl bonds leads to an increase in their strength: the values of the influence coefficient (q_{10}, q_{10}) decrease.
4. The strength of the internal and external angles of the $-CH_3$ group decreases somewhat.

From comparison of the nondiagonal coefficients (Table 1) it is easy to draw a conclusion about the character of the changes in the mutual influences of the coordinates of the different groups.

It is of interest to compare the influence coefficients of methylchlorosilanes and methylsilanes (^{14}). Replacement of methyl groups at silicon by hydrogen atoms has a smaller effect on the Si—C bond and the CSiC angle than in the case of chlorine addition, and does not affect the strength of C—H. The Si—C bond in methylsilanes is approximately 10% weaker than in the molecules of the corresponding chloro derivatives. The sign of the influence of Si—C bonds changes (coefficients (Q_1, Q_1) in Table 1 or H_{QQ}^{-1} in (^{14})). The HCH and HCSi angles in methylsilanes are somewhat stronger. In the transitions $CH_3SiCl_3 \rightarrow (CH_3)_4Si \rightarrow CH_3SiH_3$, the values of the coefficients connected with them $[(\alpha_{ij}, \alpha_{ij}), (\beta_i, \beta_i)]$ systematically decrease. The strength of the Si—Cl bond in chloro derivatives changes by larger jumps than does the strength of Si—H in methylsilanes.

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