PHYSICS

I. F. KOVALEV

1960

SovietRxiv

Abstract

Full Text

PHYSICS

I. F. KOVALEV

POTENTIAL FUNCTIONS OF MOLECULES OF THE HOMOLOGOUS SERIES $(CH_3)_nSiH_{4-n}$ $(n = 1—4)$

(Presented by Academician I. V. Obreimov, January 8, 1960)

I. The study of the properties of the simplest organosilicon compounds $(CH_3)_nSiH_{4-n}$ $(n = 1—4)$ is of theoretical and practical interest. On the basis of the method of M. V. Vol' kenshtein, M. A. El' yashevich, and B. I. Stepanov (^{1}) and L. S. Mayants (^{2,3}), we previously calculated the frequencies, forms of normal vibrations, force coefficients, and sensitivities of the frequencies to their variation for the molecules of this series. The results obtained have been partially published (^{4,5})*.

II. In the present work we give the results of calculating influence coefficients, which, as is known, have the advantage over force coefficients of being invariant under coordinate transformations. The problem was solved in a natural coordinate system for the "spectroscopic mass" of hydrogen. The coordinate designations are indicated in the scheme of the equilibrium configuration of the molecule $(CH_3)_3SiH$ (Fig. 1), as well as in work (^{4}). The system of influence coefficients was calculated by the determinant method, taking into account results obtained earlier for ethane and disilane (^{6}), and using the experimental data indicated in ($^{4-8}$). Table 1 lists only the coefficients that are nonzero.

III. Analysis of the results of calculating the frequencies and forms of vibrations, comparison of the force coefficients, influence coefficients, and comparison of these with one another and with the corresponding constants in SiH_4, Si_2H_6, and hydrocarbons (^{6}), makes it possible to draw several conclusions.

1. The distribution of forces within the molecules of the organosilicon compounds considered differs from the corresponding distribution in silanes and hydrocarbons: the force fields of the CH_3 and SiH_j $(j = 1—3)$ groups change.
2. A certain regularity is observed in the changes of the potential functions with accumulation of methyl groups at the silicon atom, on the one hand, and with a decrease in the number of Si—H bonds, on the other. The coefficient $k^{-1}_{q(1)}$ (associated with stretching of Si—H) systematically increases in

going from methylsilane to trimethylsilane in the ratio 1 : 1.02 : 1.05. The corresponding force coefficient $k_{q(1)}$ decreases. The diagonal coefficient k_δ^{-1}(H—Si—H) decreases by 44% in going from $CH_3SiH_3 \rightarrow (CH_3)_2SiH_2$, and the coefficient k_γ^{-1}(H—Si—C) by 25%. The force constants k_δ and k_γ behave oppositely. The strength of the H—Si—H and H—Si—C angles increases as the number of Si—H bonds decreases. The strength of the C—Si—C angle increases with increasing number of Si—C bonds in the ratio 1 : 1.036 : 1.045. The influence coefficient of the CH_3 group, k_a^{-1}(H—C—H), changes very little in going from methylsilane to dimethylsilane, and then, with an increase in the number of methyl groups, begins to increase. The strength of the H—C—H angle decreases. The strength of the H—C—Si angle with each substitution of an atom

---

* References to studies of methylsilanes by other authors are given in ([4,5]).

Table 1

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

Molecule	K_Q^{-1}	$k_{q(1)}^{-1}$	$k_{q(2)}^{-1}$	k_α^{-1}	k_β^{-1}	k_δ^{-1}	k_ε^{-1}	k_γ^{-1}	$h_{q(2)q(2)}^{-1}$	$H_{Qq(2)}^{-1}$	a_α^{-1}	b_α^{-1}
I. CH_3SiH_3	0,232	0,234	0,129	1,206	1,169	1,834	–	1,509	−0,003	−0,003	−0,033	0,033
II. $(CH_3)_2SiH_2$	0,236	0,239	0,129	1,205	1,209	1,278	1,174	1,206	−0,003	−0,003	−0,033	0,033
III. $(CH_3)_3SiH$	0,233	0,246	0,129	1,220	1,229	–	1,164	1,060	−0,003	−0,002	−0,034	0,034
IV. $(CH_3)_4Si$	0,231	–	0,129	1,226	1,256	–	1,123	–	−0,003	−0,002	−0,034	0,034

Molecule	a_β^{-1}	b_β^{-1}	A_β^{-1}	$A_\beta'^{-1}$	B_α^{-1}	$l_{\alpha\alpha}^{-1}$	$l_{\alpha\beta}^{-1}$	$l_{\beta\beta}^{-1}$	$o_{\alpha\beta}^{-1}$	$h_{q(1)q(1)}^{-1}$	$H_{Qq(1)}^{-1}$	H_{QQ}^{-1}	a_δ^{-1}
I. CH_3SiH_3	−0,031	0,032	−0,065	–	0,065	−0,210	−0,230	−0,191	−0,327	−0,007	−0,002	–	−0,050
II. $(CH_3)_2SiH_2$	−0,033	0,033	−0,058	−0,053	0,057	−0,212	−0,228	−0,208	−0,327	−0,009	−0,002	−0,007	−0,031
III. $(CH_3)_3SiH$	−0,034	0,034	−0,045	−0,051	0,047	−0,217	−0,227	−0,222	−0,331	–	−0,003	−0,008	–
IV. $(CH_3)_4Si$	−0,036	0,035	−0,038	–	0,038	−0,221	−0,225	−0,237	−0,334	–	–	−0,010	–

Molecule	b_δ^{-1} (b_ε^{-1})	a_γ^{-1}	b_γ^{-1}	A_γ^{-1}	B_δ^{-1} (B_ε^{-1})	B_γ^{-1}	A_ε^{-1}	$l_{\delta\delta}^{-1}$ ($l_{\varepsilon\varepsilon}^{-1}$)	$l_{\gamma\delta}^{-1}$	$l_{\gamma\gamma}^{a-1}$	$l_{\gamma\gamma}^{ab-1}$	$l_{\gamma\varepsilon}^{-1}$	$o_{\gamma\gamma}^{-1}$ ($o_{\gamma\varepsilon}^{-1}$)
I. CH_3SiH_3	0,069	−0,077	0,054	−0,054	0,054	–	–	−0,576	−0,319	−0,413	–	–	–
II. $(CH_3)_2SiH_2$	(0,047)	−0,069	0,061	−0,052	0,053	0,041	−0,031	–	−0,301	−0,344	−0,082	−0,275	−0,204
III. $(CH_3)_3SiH$	(0,070)	−0,070	–	−0,071	(0,037)	0,015	−0,040	(−0,133)	–	–	−0,081	−0,334	(0,231)
IV. $(CH_3)_4Si$	–	–	–	–	(0,042)	–	−0,042	(−0,249)	–	–	–	–	–

Molecule	$o_{\gamma\delta}^{-1}$ ($o_{\delta\varepsilon}^{-1}$)	$o_{\delta\varepsilon}^{-1}$	C_β^{-1}	D_β^{-1}	e_β^{-1}	d_β^{-1}	$d_\beta'^{-1}$ ($D_\beta'^{-1}$)	s_β^{-1}	v_β^{-1}	$v_\beta'^{-1}$	u_β^{-1}	t_β^{-1} ($l_{\alpha\delta}^{-1}$)	(Q_1, α_{48})
I. CH_3SiH_3	−0,044	–	–	–	−0,001	0,002	–	–	–	–	–	(0,022)	–
II. $(CH_3)_2SiH_2$	(−0,075)	–	0,005	0,002	0,001	−0,004	0,003	0,010	0	–	0	(0,017)	−0,003
III. $(CH_3)_3SiH$	–	–	0,007	0,003	0,003	−0,005	(−0,003)	0,005	−0,001	−0,003	−0,002	−0,004	−0,003
IV. $(CH_3)_4Si$	–	−0,128	0,008	−0,003	–	–	–	0,012	0,001	–	0,003	−0,006	−0,002

Table 1 (continued)

Molecule	4: (Q_1, α_{56})	4: $m_{\beta\gamma}^{-1}$	4: $n_{\beta\gamma}^{-1}$	4: $m_{\beta\varepsilon}^{-1}$	4: $n_{\beta\varepsilon}^{-1}$	4: $n_{\beta\varepsilon}'^{-1}$	4: ($n_{\beta\gamma}'^{-1}$)	4: d_γ^{-1}	4: $d_\gamma'^{-1}$	4: c_ε^{-1}	4: d_ε^{-1}	4: $p_{\alpha\gamma}^{-1}$	4: $r_{\alpha\gamma}^{-1}$	4: $p_{\beta\gamma}^{-1}$
I. CH_3SiH_3	–	0,044	0,010	–	–	–	0	0,002	–	–	–	−0,023	−0,021	–
II. $(CH_3)_2SiH_2$	−0,003	0,031	0,044	−0,112	0,032	(0,002)	0,001	0	0,002	0,004	−0,003	−0,026	−0,027	−0,022
III. $(CH_3)_3SiH$	−0,002	0,015	0,038	−0,116	0,053	0,030	0,002	–	0,001	0,004	−0,002	−0,029	−0,031	0,005
IV. $(CH_3)_4Si$	−0,001	–	–	−0,123	0,058	–	–	–	–	0,006	−0,003	–	–	–

Molecule	4: $r_{\beta\gamma}^{-1}$	4: $r_{\beta\gamma}'^{-1}$	4: $p_{\alpha\varepsilon}^{-1}$	4: $r_{\alpha\varepsilon}^{-1}$	4: $r_{\alpha\varepsilon}'^{-1}$	4: ($p_{\beta\delta}'^{-1}$)	4: ($r_{\beta\delta}^{-1}$)	4: ($r_{\beta\varepsilon}^{-1}$) α_{13}	4: (γ, α_{299})	4: (γ, α_{299})	4: $(\varepsilon, \alpha_{1213})$	4: $(\varepsilon, \alpha_{2313})$	4: (β, α_{713})	4: $(\beta, q_{97}, \gamma_1)$
I. CH_3SiH_3	–	–	–	–	–	−0,019	−0,023	–	–	–	–	–	–	–

Fig. 1. Equilibrium configuration of the molecule $(CH_3)_3SiH$

Figure 1: Fig. 1. Equilibrium configuration of the molecule $(CH_3)_3SiH$

Molecule	4: $r_{\beta\gamma}^{-1}$	4: $r_{\beta\gamma}'^{-1}$	4: $p_{\alpha\varepsilon}^{-1}$	4: $r_{\alpha\varepsilon}^{-1}$	4: $r_{\alpha\varepsilon}'^{-1}$	4: $(p_{\alpha\delta}'^{-1})$	4: $(p_{\beta\delta}^{-1})$	4: $(r_{\beta\varepsilon}^{-1})$	4: $(\alpha_{13}, \gamma_{99})$	4: $(\alpha_{12}, \gamma_{99})$	4: $(\varepsilon_{12}, \alpha_{13})$	4: $(\varepsilon_{12}, \alpha_{23})$	4: (β_{7}, α_{13})	4: (β_{7}, γ_1)
II. $(CH_3)_2SiH_2$	0,016	−0,020	0,023	0,012	(−0,024)	0,008	−0,023	0,010	0,007	–	–	0,002	−0,002	−0,002
III. $(CH_3)_3SiH$	0,018	−0,027	0,019	0,008	0,006	(−0,021)	(0,001)	0,001	0,003	0,007	0,006	0,001	−0,02	0,001
IV. $(CH_3)_4Si$	–	–	0,011	−0,002	–	(−0,008)	(0,008)	–	–	−0,002	−0,003	0,001	−0,001	–

Notes. 1. The influence coefficients are arranged in the table in the following order: 1–diagonal; 2–referring to interactions of the coordinates of the group Si—CH_3; 3–the same for the group $C(SiH_n)C_{3-n}$ ($n = 0, 3$); 4–referring to interactions of the coordinates of the groups Si—CH_3 and $C(SiH_n)C_{3-n}$ with one another.

2. Mostly standard notation has been used ([1,4,5]). Capital letters refer to interactions of the Si—C bond with the corresponding coordinates. The interacting coordinates indicated in parentheses are denoted with reference to the scheme of the molecule $(CH_3)_3SiH$. The numbers in parentheses correspond to the coefficients written in parentheses. $l_{\gamma\gamma}^{a-1}$ is the coefficient of mutual influence of the angles H—Si—C having the common side Si—C; $l_{\gamma\gamma}^{ab-1}$ is that of angles having the common side Si—H; $l_{\alpha\delta}^{-1}$ denotes the mutual influence of the angles H—C—H and H—Si—H.

hydrogen of the methyl group also decreases by 2-3%, while the strength of the C–H bond is the same for all methylsilanes and is approximately twice the strength of Si–H. The strength of Si–C changes hardly at all; comparison with ethane and disilane shows that this bond is considerably stronger than Si –Si (~70%), but less strong than C–C (~50%). Table 1 gives a clear idea of the magnitude of the mutual influence of the coordinates for the series of compounds considered.

Fig. 1. Equilibrium configuration of the molecule $(CH_3)_3SiH$

3. A certain difference is observed in the magnitude of the force interaction of identical pairs of coordinates arranged in the same way with respect to one another, but having different orientations with respect to other coordinates. For example, the interactions ε_{12} with α_{13} and α_{23} are not equal (see Fig. 1): the electron cloud is asymmetric with respect to the plane $H_3C_1SiC_2H_5$. The corresponding influence coefficients in the table are denoted by identical letters, but are distinguished by a prime ($r_{\alpha\varepsilon}^{-1}$ and $r_{\alpha\varepsilon}'^{-1}$; also A_{β}^{-1} and $A_{\beta}'^{-1}$, d_{β}^{-1} and $d_{\beta}'^{-1}$, etc.).

4. Methylsilanes possess only two values of the characteristic C—H frequencies: ~2900 and ~2967 cm^{-1}.
5. The stretching frequencies Si—H depend strongly only on the parameters $k_{q(1)}$ and $h_{q(1)q(1)}$, depend very little on $H_{Qq(1)}$, b_ε, a_γ, and b_γ, and do not depend on the remaining parameters.
6. The asymmetric deformation vibrations H—C—H (region ~1430 cm^{-1}) are fairly characteristic of the coordinate groups α and β; the symmetric ones (~1260 cm^{-1}) are additionally connected with changes in Q, δ, and γ. The remaining vibrations are also connected with changes in many coordinates.

Saratov State
Pedagogical Institute

Received
8 I 1960

References Cited

1. M. V. Vol' kenshtein, M. A. El' yashevich, B. I. Stepanov, *Vibrations of Molecules*, 1, Moscow-Leningrad, 1949.
2. L. S. Mayants, *Transactions of the P. N. Lebedev Physics Institute, Academy of Sciences of the USSR*, **5**, 65 (1950).
3. L. S. Mayants, *Optics and Spectroscopy*, **5**, 378 (1958).
4. I. F. Kovalev, *Optics and Spectroscopy*, **4**, 560 (1958).
5. I. F. Kovalev, *Optics and Spectroscopy*, **6**, 594 (1959).
6. I. F. Kovalev, *Optics and Spectroscopy*, **3**, 552 (1957).
7. H. Westermark, *Acta Chem. Scand.*, **9**, 947 (1955).
8. E. A. V. Ebsworth, M. Onyszchuk, N. Sheppard, *J. Chem. Soc.*, 1958, 4, 1453.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.