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Mean Square Amplitudes and Force Constants of Silicon Tetrachloride and Sulfur Dichloride

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The atomic distances of the $SiCl_4$ and SCl_2 molecules and their root-mean-square amplitudes of thermal vibration were measured by the sector-microphotometer method of electron diffraction. The general force constants were calculated by the use of the fundamental frequencies together with the mean square amplitudes thus obtained. The fundamental frequencies of the free molecules were obtained for $SiCl_4$ from the Raman spectrum in the gaseous state and for SCl_2 from the infrared spectrum in the gaseous state.

The intramolecular potential is one of the most fundamental properties of molecules. Almost all the phenomena in chemistry are, more or less, related to the potential function of molecules. The force field between atoms in molecules have usually been obtained by the analysis of the vibrational spectra, but the number of the observed frequencies is not always enough to determine all the force constants in the general quadratic form. For instance, even for such a simple molecule as SCl_2, four force constants must be fixed, but three frequencies are to be observed. For $SiCl_4$ four frequencies are observed for five unknown force constants. Thus with the frequencies alone a unique solution of the force field cannot be attained. The difficulty is usually avoided either by the use of some additional isotopic effect on the vibrational spectra, or of some additional assumption such as the Urey-Bradley force system to reduce the number of unknown parameters. The root-mean-square amplitude, which is obtained by the sector-microphotometer technique of electron diffraction, has a close connection with the potential function, so that it may be used as such an additional information. In fact, the force constants of the CCl_4 and $GeCl_4$ molecules were determined by such a consideration[1]. In this report the result of the application of the same method to the $SiCl_4$ and SCl_2 molecules will be described.

These two molecules have an advantage that the correction to the failure of the Born approximation is negligibly small, since the atomic number of the atoms composing the molecules are very close. It is most favourable for getting accurate values of the mean square amplitudes to save the consideration on one of the tedious corrections.

The force field of the $SiCl_4$ molecule was considered by Shimanouchi[2] by the use of the Urey-Bradley assumption, whereas that of the SCl_2 molecule has never been studied.

Silicon tetrachloride

The diffraction apparatus used and the analytical procedure applied are quite the same as those reported in the preceding paper[1] except a few improvements. The first improvement is to use a needle-type nozzle besides the drum-type one which has been used. The nozzle is made of a stainless steel tube of the inner diameter of 0.55 mm. It gives better values of the mean square amplitudes than the drum-type one, because the distribution of gas molecules is concentrated into a narrower region.

The second improvement is to have measured the gas distribution at the diffraction center and have made a definite correction for the effect. In the theoretical calculation an assumption is made that the diffraction occurs at a single point, but in the practical experiment the electron beams are diffracted in some finite region of the cross section of electron beams with the gas stream. Thus the diffraction halos spread out more than those calculated theoretically. It leads to an apparent increase in the mean square amplitudes over the theoretical values. In

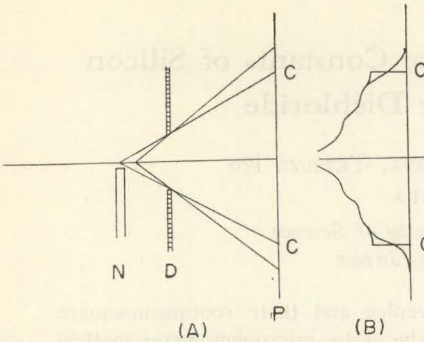

Fig. 1. Measurement of gas distribution.
(A) Schematic arrangement in the camera, N: nozzle, D: diaphragm, P: plate.
(B) Intensity distribution on the photographic plate.

order to measure the gas distribution a diaphragm with a circular aperture is put between the nozzle and the photographic plate as schematically shown in Fig. 1. If the diffraction occurs at a point just as assumed in the theoretical calculation, the diffraction halos are sharply cut off at a point C on the photographic plate, and no blackness beyond it. However, if the diffraction occurs in some finite range along the primary beam, some diffracted electron beams come beyond the point C and a gradual change of the diffraction intensity would be observed around the point C. By measuring the angular dependence of the intensities in the photographs with and without the diaphragm, the gas distribution at the center was estimated. It was found from the distribution of gas molecules that the apparent increase in the mean amplitudes are 0.0009Å and 0.0013Å for the Si-Cl and Cl···Cl pairs, respectively.

The least-squares calculation was carried out on the molecular intensity curves, using five unknown parameters: two atomic distances, r(Si-Cl) and r(Cl···Cl), two mean square amplitudes l(Si-Cl) and l(Cl···Cl), and the index of resolution i. The final results obtained as the average of the four photographs are summarized in Table I. The limits of errors were taken as 2.5 times of the standard deviations obtained in the least-squares calculation plus the estimated systematic errors. 2.5 times of the standard deviation means to include 99% of the observations in the range indicated.

Table I. Interatomic distances and mean amplitudes of SiCl$_4$ at 20°C.

	Si-Cl	Cl···Cl
r_g	2.017±0.005 Å	3.292±0.008 Å
l_e	0.0471±0.0025 Å	0.0856±0.0025 Å
i	1.03±0.03	

Finally the Raman spectrum of SiCl$_4$ in the gaseous state was measured. For the calculation of the force constants, the normal frequencies of free molecules must be used. Unfortunately for SiCl$_4$ the Raman spectrum is available only in the liquid state[3]. The infrared spectrum in the gaseous state has been measured[4], but it provides us with the frequency of ν_3 alone, because another infared-active frequency ν_4 is too small in frequency to be observed by the usual prism spectrometer. The apparatus and the experimental procedure for taking the Raman spectrum are essentially the same as those used for the Raman spectrum of the gaseous carbon tetrachloride[5]. The fundamental frequencies thus obtained are listed in Table II. It is noticed that the frequencies in the gaeous state are very close to those in the liquid state except the frequency ν_3, which is larger in the gaseous state. It is in good accord with the results on similar tetrahedral molecules such as CCl$_4$[6] and CF$_4$[7].

Table II. Fundamental frequencies of SiCl$_4$ in cm^{-1} unit.

	Raman(gas)	Infrared(gas)	Raman(liquid)
ν_1	425±1		424
ν_2	149±2		150
ν_3	621±5	619.5±1	610
ν_4	220±4		221

Rigorously speaking, for the calculation of the force field the normal frequencies must be used instead of the fundamental frequencies. However, the differences between them must be neglected because no knowledge on the anharmonic terms of the vibrations is available at present and, in addition, the correction is considered to be of the order of magnitude of the errors indicated above.

Now, as already described, the four observed frequencies are not enongh to determine all the force constants. It follows that the two mean square amplitudes compatible with the four frequencies are not fixed to definite values but they have one degree of freedom: in other words, the mean amplitudes calculated with the four frequencies are represented by an ellipse on the plane of the two mean amplitudes, as shown in Fig. 2. Taking into account the errors in the values of the frequencies, the calculated values are found in a narrow area, as shown in Fig. 2. On the other hand the observed values of the mean amplitudes are represented by the region enclosed by the limits of errors. Therefore the overlapping area provides us with the reasonable values of the force constants consistent both with the spectra and the mean amplitudes. The force constants thus determined are shown in Table III, together with the uncertainties which denote the range of the values allowed by the overlapping area. It would be worth while to note that the uncertainty of the final values of the force constants come from those of the mean amplitudes as well as from those of the frequencies by almost the same order of magnitude. It is easily seen that the force constants thus obtained are of reasonable magnitude, as shown in Table IV, when compared with those of the CCl_4 and $GeCl_4$ molecules previously determined[1].

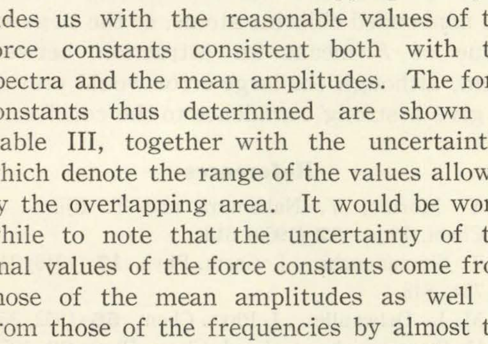

Fig. 2. Correlation curve of two mean amplitudes of $SiCl_4$.

Table III. Force constants of $SiCl_4$ in md/A unit at 20°C.

symmetry coordinate system		internal coordinate system	
F_{11}	3.77±0.02	k_r	3.5±0.7
F_{22}	0.154±0.004	k_{rr}	0.1±0.2
F_{33}	3.4±0.9	k_α-$k_{\alpha\alpha'}$	0.25±0.04
F_{34}	0.4±0.4	$k_{\alpha\alpha}$-$k_{\alpha\alpha'}$	0.05±0.02
F_{44}	0.25±0.04	$k_{r\alpha}$-$k_{r\alpha'}$	0.3±0.3

Table IV. Comparison of force constants of tetrahedral molecules in md/Å.

	CCl_4	$SiCl_4$	$GeCl_4$
k_r	3.59±0.56	3.5±0.7	2.79±0.23
k_{rr}	0.24±0.19	0.1±0.2	0.16±0.08
k_α-$k_{\alpha\alpha'}$	0.38±0.03	0.25±0.04	0.18±0.01
$k_{\alpha x}$-$k_{\alpha\alpha'}$	0.03±0.01	0.05±0.02	0.03±0.01
$k_{r\alpha}$-$k_{r\alpha'}$	0.36±0.15	0.3±0.3	0.09±0.14

Sulfur dichloride

The same method of analysis was applied to the diffraction photographs of SCl_2. The correction for the finite sample size, which was serious to the calculation of the mean amplitudes, was found to be −0.0017Å and −0.0023Å for S-Cl and Cl···Cl pairs, respectively. The results obtained as the average of the four sets of leastsquares analysis of the molecular intesity curves are shown in Table V. In this case too, five unknown parameters were assumed for the analysis.

The most serious difficulty for determining the force field of this molecule is the accuracy of the vibrational frequencies. Herndon analysed the infrared spectra in the gaseous state[8] to get the fundamental frequencies. In order to check his result the infrared spectrum in the gaseous state was again studied. Although a number of facts against Herndon's argument were found, our final assignment is quite similar to that by Herndon, only with slight differences in wave numbers: $\nu_1=520\pm20\,\mathrm{cm}^{-1}$, $\nu_2=202\pm7\,\mathrm{cm}^{-1}$, and $\nu_3=524\pm5\,\mathrm{cm}^{-1}$. In this analysis the Raman spectrum in the liquid state by Stammreich[4] is also taken into consideration. The large uncertainty given to the

Table V. Interatomic distances and mean amplitudes of SCl_2 at 20°C.

	S-Cl	Cl···Cl
r_g	2.006±0.004Å	3.143±0.009Å
l_e	0.053±0.004Å	0.102±0.007Å
i	0.92±0.05	
∠Cl-S-Cl	103.0°±0.4°	

symmetric stretching frequency, ν_1, comes from the fact that the band is considered to be covered by the strong antisymmetric stretching band ν_3.

For computing the F matrix of sulfur dichloride from the three frequencies the same situation is encountered as that in the case of silicon tetrachloride. The mean amplitudes compatible with the three frequencies are shown by a narrow strip in Fig. 3. The force constants obtained from the overlapping region of the narrow strip with the ellipse of the observed values are listed in Table VI. It is a fortunate fact that the two mean amplitudes of this molecule are influenced not heavily by ν_1, but rather by ν_2. Therefore the large uncertainty of the frequency does not affect the final values of the force constants so seriously. The most striking feature of this set of the force constants is the negative values of F_{12}, $k_{r\alpha}$, or the F term in the Urey-Bradley force system. F denotes the force between the nonbonded chlorine atoms, so the negative value of F means an attraction between them, although the large error would prevent to give a strong confidence to the conclusion.

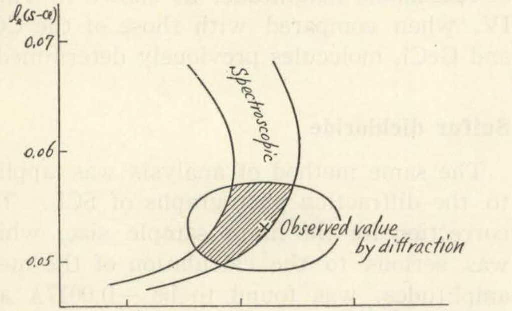

Fig. 3. Correlation curve of two mean amplitudes of SCl_2.

Table VI. Force constants of SCl_2 in md/A unit at 20°C.

Symmetry coordinate system	Internal coordinate system	Urey-Bradley force system
F_{11} 1.8±0.5	k_r 2.1±0.3	K 2.34±0.32
F_{12} −0.25±0.10	k_{rr} −0.3±0.3	H 0.67±0.48
F_{22} 0.45±0.15	$k_{r\alpha}$ −0.18±0.07	F −0.44±0.35
F_{33} 2.4±0.1	k_α 0.45±0.15	F' 0.08±0.38

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DISCUSSION

S. J. CYVIN: Force constants are not very much sensitive to small changes in mean amplitudes. Hence a very high precision in the measurements is required for computing force constants by means of the mean amplitudes. From this point of view the presented results of Prof. Morino and collaborators are remarkably nice.

Y. MORINO: For the comment made by Dr. Cyvin I would like to remind you of my statement that the influence of the accuracy of the mean amplitudes on the force constants is almost of the same order of magnitude as that of the accuracy of the observed frequencies.

K. HEDBERG: Based on Dr. Iwasaki's and my experience with PCl_3, for which we carried out calculations similar to those described by Prof. Morino, we feel that some caution is in order in respect to the significance we attach to derived potential constants. The effect of uncertainty in factors such as f values, blackness correction, etc., may be to change the mean amplitudes several percent; this changes the values of the derived constants significantly, (but perphaps not unreasonably). A not infrequent result is to obtain imaginary values for constants if the experimental values for frequencies and amplitudes are employed; this is perhaps an indication that all is not well.

Y. MORINO: We have estimated every systematic error for the measurement of the mean amplitudes. For the error due to the finite sample size, which was the most serious, we measured the gas distribution and made a correction to the effect. For the $D-E$ calibration we took photographs below $D=0.5$. The linear relation between D and E in this range had been established by a preliminary experiment.

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Out-of-Plane Molecular Vibrations and "Shrinkage Effects" in Naphthalene Skeleton

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Spectroscopic calculations have been performed for the out-of-plane vibrations of the naphthalene skeleton. The molecule has been treated as a ten-particle, planar regular structure X_2Y_8($X=C$, $Y=CH$). Small harmonic vibrations were assumed. The two linear shrinkage effects have been estimated with the following results referring to 298°K: 0.0073Å for the shorter distance (2-7), and 0.0067Å for the longer distance (1-6). Recent electron-diffraction measurements on naphthalene due to Bastiansen *et al.* are quoted, and certain refinements of their results are discussed.

By the increasing accuracy of electron-diffraction experiments Bastiansen *et al.* have observed a shortening of long interatomic distances in linear chains, referred to as the shrinkage effect[1]. This effect is tentatively explained by considering the molecular vibrations, and may accordingly be calculated spectroscopically by the method of Morino[2], using the generalized mean-square amplitudes[3]. As pointed out by Professor Bastiansen, the same method may be applied to any linear conformation of three atoms in a molecule, e.g. a condensed aromatic. In connection with the recent electron-diffraction investigations of condensed aromatics in the gaseous state[4] even a rough estimate of the shrinkage effects from spectroscopic data would be very useful.

The purpose of the present work was to estimate the order of magnitude of the two different shrinkage effects in naphthalene skeleton, to see if the influence of molecular vibrations could be neglected with confidence. Next it was intended, if possible, to make the first step towards a correction for intramolecular motion of the electron-diffration results on naphthalene. It had been decided to start with the out-of-plane vibrations for two reasons: (i) The theoretical treatment is simpler than that of the in-plane vibrations. (ii) They were believed to give the largest and possibly the main contribution to the shrinkage effects.

Spectroscopic calculations. The spectroscopic computations are based on the usual assumption of small harmonic vibrations[5]. The naphthalene molecule is treated as a ten-particle planar structure X_2Y_8($X=C$, $Y=CH$) with two regular hexagonal rings in the equilibrium position. For the numbering of

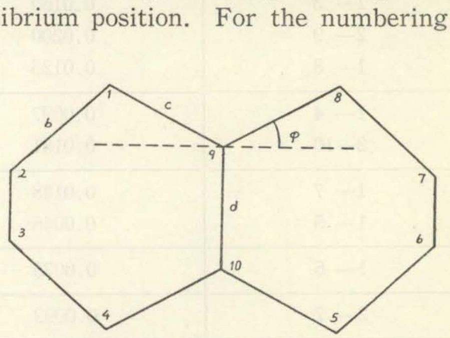

Fig. 1. Numbering of atoms and structural parameters of naphthalene skeleton.