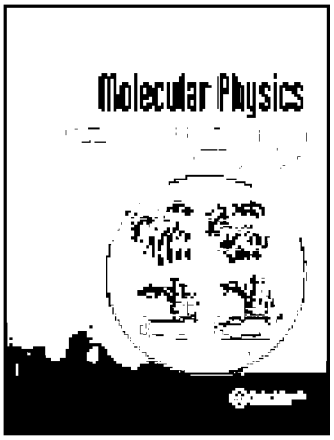

Molecular Physics: An International Journal at the Interface Between Chemistry and Physics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tmph20

Structural studies of tetrachloride liquids

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Published online: 23 Aug 2006.

To cite this article: J.R. Granada , G.W. Stanton , J.H. Clarke & J.C. Dore (1979) Structural studies of tetrachloride liquids, Molecular Physics: An International Journal at the Interface Between Chemistry and Physics, 37:4, 1297-1304, DOI: 10.1080/00268977900100931

To link to this article: http://dx.doi.org/10.1080/00268977900100931

MOLECULAR PHYSICS, 1979, VOL. 37, No. 4, 1297–1304

Structural studies of tetrachloride liquids
III. Molecular structure of CCl_4, $SiCl_4$, $TiCl_4$, $GeCl_4$ and $SnCl_4$

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(*Received* 7 *August* 1978)

The differential scattering cross-sections for neutrons scattering by liquid CCl_4, $SiCl_4$, $TiCl_4$, $GeCl_4$ and $SnCl_4$ at 20°C have been obtained using the pulsed neutron beam from the Harwell Linac. The measured data at two scattering angles (150° and 90°) have been analysed using a molecular form factor with wavelength-dependent Debye–Waller factors. Molecular bond length parameters extracted from a χ^2-fit to the observations are compared with data obtained by other techniques. Special consideration is given to the calibration of the momentum-transfer scale and the data are found to be sensitive to the variation of mean emission times for different wavelength neutrons leaving the moderator material. Correction for this effect gives an improved fit to the form factor but does not alter the fitted bond length values.

1. INTRODUCTION

In paper I of this series [1, 2], pulsed neutron diffraction measurements were reported for liquid carbon tetrachloride. Three fixed detectors were used to record the scattered neutrons over an incident wavelength range of 0·2–3·5 Å corresponding to a momentum transfer range of 2–60 $Å^{-1}$. The observed diffraction pattern for the Q-range of 6–28 $Å^{-1}$ was analysed in terms of a molecular form factor which contained wavelength-dependent Debye–Waller factors. An excellent fit to the data was obtained and the molecular bond length was defined to a high accuracy ($\pm 0{\cdot}002$ Å). Some systematic discrepancies were noted in the fit at high Q-values which indicated the possibility of anharmonic effects in the vibrational motion or alternatively a non-linear variation in the Q-scale calibration resulting from the time-of-flight measurement. In the present paper the study is extended to include other tetrachloride systems ($SiCl_4$, $TiCl_4$, $GeCl_4$ and $SnCl_4$) and the apparent discrepancies in the high Q-value region are re-examined in terms of the variation in neutron flight-time caused by the fact that different wavelength neutrons do not emerge from the moderator at the same initial time.

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2. Experimental procedure and data reduction

The measurements were made with the total scattering spectrometer (TSS) at the Harwell Electron Linac. The samples were contained in flat plate containers using vanadium foil windows of 0·1 mm thickness. The liquid sample was nominally 4 mm thick and the experiment was conducted in the same manner as previously described [1]. Data reduction was made using the LINDA program [3] and the routine corrections for container scattering, absorption, multiple-scattering, etc. were applied in the usual manner ; relevant neutron parameters for these liquids are given in table 1 with other physical properties.

Table 1. Physical properties and neutron parameters for the various tetrachloride liquids used in the present experiments ; ρ_N is the molecular number density.

XCl_4	b_x/fm	σ_i/barns	σ_{sc}/barns	σ_{abs}†/barns	ρ/g cm^{-3}	ρ_N/ Å^{-3} × 10^{-3}
CCl_4	6·648	23·69	75·36	75·19	1·587	6·213
$SiCl_4$	4·149	23·70	71·98	75·19	1·483	5·26
$TiCl_4$	−0·337	26·52	74·07	78·41	1·726	5·48
$GeCl_4$	8·186	23·78	78·32	76·58	1·844	5·18
$SnCl_4$	6·220	23·71	74·69	75·24	2·226	5·15
Cl	9·579	5·92				

† Absorption cross sections are quoted for a wavelength of 1 Å.

Some problems were encountered with the subtraction of the background count for the 150° counters and the results for CCl_4 were used to provide a satisfactory procedure. The additional corrections resulted in minor changes to the overall level of the cross-section in the high Q-value region and did not

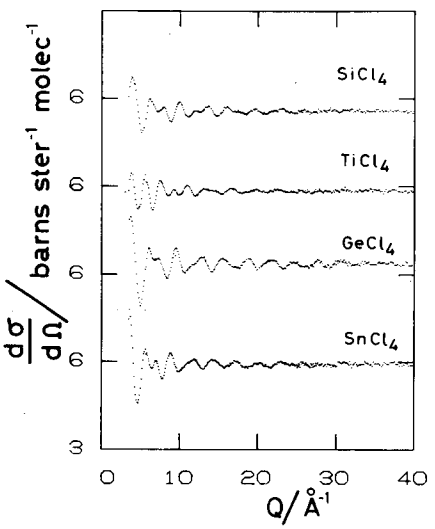

Figure 1. The total scattering differential cross-sections for various tetrachloride liquids observed at 150° scattering angle.

affect the oscillatory form of the diffraction pattern. The observed cross-sections for the 150° detector bank are shown in figure 1 as a function of the scattering vector, Q.

3. Data analysis

Since the contributions to the cross-section from intermolecular terms are negligible [1] above a Q-value of 7 Å^{-1}, the observed oscillatory structure results from interference effects within the single molecular unit and is characterized by a molecular form factor $f_1(Q)$ which may be written for a tetrahedral molecule XCl_4 as :

$$f_1(Q)=\frac{1}{(b_x+4b_{Cl})^2}\,[b_x{}^2+4b_{Cl}{}^2+8b_xb_{Cl}j_0(Qr_{XCl})\exp(-\gamma_{XCl}Q^2) + 12b_{Cl}j_0(Qr_{ClCl})\exp(-\gamma_{ClCl}Q^2)], \quad (3.1)$$

where b_x and b_{Cl} are the coherent scattering lengths for the X and Cl nuclei respectively ; the bond lengths r_{XCl} and r_{ClCl} are related by $r_{ClCl}=2\sqrt{(2/3)}r_{XCl}$ and the exponential term is a Debye–Waller factor in which γ is related to the mean square amplitude of vibration $\langle u^2\rangle$. In paper I, it was shown that a good fit to the data was obtained with a three parameter expression of the form :

$$\gamma=\gamma_0(\alpha+k_\lambda\lambda^n)\,; \quad \gamma_0=\tfrac{1}{2}\langle u^2\rangle, \quad (3.2)$$

for each of the oscillatory terms. Although the individual parameters were not well defined it was found that the bond length parameter r_{XCl} was relatively insensitive to parameter variation. This is due to the fact that the γ-factor influences the amplitude of the oscillations but r_{XCl} is defined mainly by the position of the cross over points on the Q-scale.

The present results, which were obtained before the measurements reported in the earlier paper [1], do not have the same statistical accuracy but permit a systematic study of the $f_1(Q)$ behaviour with variation of the central atom in the tetrachloride unit. In order to isolate this variation it was found possible to fix the values $\alpha=1$ and $n=1{\cdot}8$ which gave satisfactory χ^2 minima for all the samples and are consistent with the previous findings [1] for CCl_4. However a distinct improvement to the fit was observed when the k_λ values for the two terms in the molecular form factor (k_{XCl} and k_{ClCl}) (equations (3.1) and (3.2)) were decoupled. The χ^2-optimization routine was therefore carried out with the three parameters, r_{XCl}, k_{XCl} and k_{ClCl}. The results are shown in table 2 for both 150° and 90° detectors. If the restrictions imposed on the α and n values were removed, there was an insignificant change in χ^2 and the r_{XCl} value remained constant to better than 0·001 Å.

The precision in the r_{XCl} value (defined by a 10 per cent change in χ^2) is dependent on the observed magnitude of the oscillations in the diffraction pattern. This varies for the different samples (figure 1) due to the change in b_x and also due to the apparent damping of the ClCl contribution caused by the k_{ClCl} terms. This seems to be a systematic effect as the high values for $SiCl_4$ and $GeCl_4$ and corresponding low values for $TiCl_4$ and $SnCl_4$ are well reproduced in the data for both scattering angles ; in all cases $k_{XCl}>k_{ClCl}$. The larger values of k_{ClCl} for CCl_4 and $SiCl_4$ also correspond to reduced mass of the central

Table 2. The parameters resulting from χ^2-optimization of the $f_1(Q)$ fit to the observed diffraction pattern for various tetrachloride liquids. Case (*a*) corresponds to the direct expressions (equations (3.1) and (3.2)) with $\alpha = 1$ and $n = 1{\cdot}8$; case (*b*) includes a correction for the neutron mean emission time (§ 3.2).

XCl_4	θ	Case	k_{XCl}	k_{ClCl}	r/Å	χ^2
$GeCl_4$	150°	*a*	1·9	0·9	2·110	33·8
		b	1·9	0·8	2·109	22·5
	90°	*a*	2·0	1·3	2·107	152·0
		b	2·0	1·3	2·105	134·9
$TiCl_4$	150°	*a*	2·3	0·7	2·169	9·5
		b	2·2	0·7	2·168	8·1
	90°	*a*	1·7	1·0	2·180	60·9
		b	1·6	1·0	2·177	59·3
$SiCl_4$	150°	*a*	1·8	1·4	2·014	17·4
		b	1·8	1·4	2·014	13·7
	90°	*a*	1·6	1·0	2·014	132·1
		b	1·7	0·9	2·013	122·4
$SnCl_4$	150°	*a*	1·9	0·6	2·286	27·5
		b	1·9	0·6	2·285	25·5
	90°	*a*	1·7	0·8	2·292	107·2
		b	1·8	0·8	2·289	101·6

Table 3. Comparison of the observed molecular bond lengths (r_{XCl}) determined from different diffraction experiments: e, electron; X, X-ray; n(R), neutron (reactor); n(L), neutron (linac). (N.B. error estimates in reference [7] seem to involve a different criterion from that adopted in the present paper.)

XCl_4	r_{X-Cl}/Å	Reference	Method
$GeCl_4$	2·112 ± 0·001	[4]	e
	2·16	[5]	x
	2·109 ± 0·004	This work	n(L)
$TiCl_4$	2·169 ± 0·002	[6]	e
	2·159 ± 0·001	[7]	n(R)
	2·169 ± 0·004	This work	n(L)
$SiCl_4$	2·018 ± 0·003	[8]	e
	2·06	[9]	x
	2·012 ± 0·001	[7]	n(R)
	2·014 ± 0·004	This work	n(L)
$SnCl_4$	2·281 ± 0·004	[10]	e
	2·30	[5]	x
	2·288 ± 0·001	[7]	n(R)
	2·286 ± 0·005	This work	n(L)

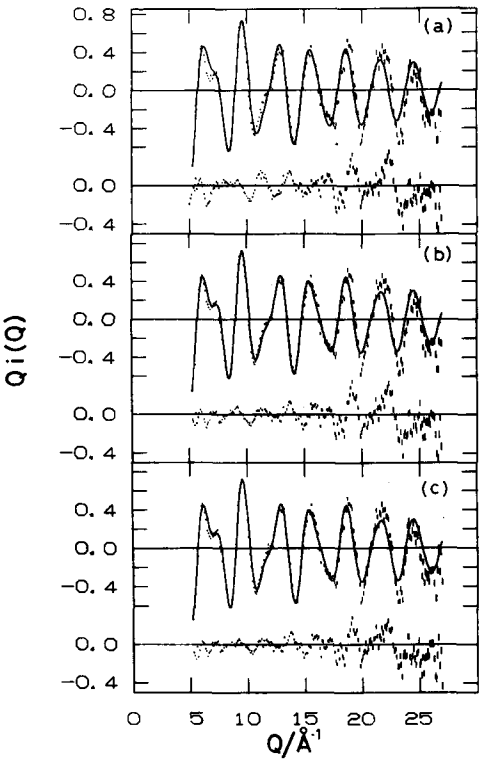

Figure 2. χ^2-fits and residual functions for 150° data of $GeCl_4$ (*a*) constrained fit with $k_{Cl}=k_X$; (*b*) three-parameter fit with $k_{Cl}\neq k_X$; (*c*) as (*b*) but with corrections for neutron mean emission time.

atom and higher energies for excitation of vibrational modes of the molecule so that the observed variation can probably be more fully explained in terms of inelastic neutron scattering effects. The derived r_{XCl} values are compared with the results of other measurements in table 3 ; the values are quoted for the direct observation (r_a) without correction for vibrational effects. It can be seen that the agreement is satisfactory in all cases although no recoil corrections [1] have been applied to the data. An example illustrating the quality of the fits is given in figure 2 for $GeCl_4$; the first curve is obtained with the restriction $k_{Cl}=k_X$ and the second curve with this restriction removed. The improvement in the fit is particularly clear for the double peak at 6 $Å^{-1}$ and the shoulder at 12 $Å^{-1}$ which are not well reproduced with the restricted conditions. The lower curve is obtained for a modified Q-scale calibration which is considered in the next section.

Q-scale calibration

It is notable that all data sets show an apparent displacement of the oscillatory pattern relative to the computed $i(Q)$ curve for Q-values greater than 20 $Å^{-1}$. This effect was also observed in the earlier measurements for CCl_4 and a more detailed analysis has now been carried out. It is known that the effective time of neutron emission from the moderator is dependent on neutron energy.

Carpenter [11] has presented data for various moderator assemblies in a recent comprehensive paper on pulsed neutron techniques. The wavelength dependence of the neutron mean emission time indicates that the true time-of-flight cannot be obtained from a fixed initial time delay τ_0 used in calculating the elastic Q-value by

$$Q=\frac{(L_0+L_1)\sin\theta/2}{(\tau_0+t)}.$$

The variation in $\tau_0(\lambda)$ causes the fast (epithermal) neutrons to be emitted more promptly than the slow (thermal) neutrons. Since the Q-scale is calibrated using Bragg scattering from a powder [3, 12], τ_0 is effectively measured for the wavelength range 1·2–3·5 Å at 150° and 0·8–2·9 Å at 90°. If a constant value is used, neutrons in the short wavelength region have an apparent flight-time which is shorter than the actual flight-time and consequently the Q-value corresponding to that time channel is over-estimated. This results in the displacement observed in the experimental data. Application of an anharmonicity term [1] produces a similar non-linearity in the Q-scale and explains the improved value of χ^2 obtained in the earlier analysis of the CCl_4 data but the variation of mean emission time is a more plausible explanation of the effect and does not result in an increased value of r_{XCl}.

In the high energy limit [11], Carpenter has shown that the mean emission time $\tau(\lambda)$ and the pulse width (standard deviation on time of emission) are proportional to wavelength. We may therefore account for the variation in the short wavelength (high-Q) region by writing

$$\tau_0(\lambda)=k_T\lambda\,;\quad \lambda<\lambda_0, \tag{3.3}$$

where k_T is a constant and λ_0 is an arbitrary cut-off point. The value of λ_0, which is greater than 1 Å, has very little effect on the data as the small change in τ_0 does not alter the Q-value significantly for long flight-times. When this expression was incorporated into the fitting procedure the χ^2 values were reduced for all cases and gave a value of 7 ± 2 μs Å^{-1} for k_T. This improvement was particularly apparent in the data for CCl_4 which have a higher statistical accuracy than the other measurements. The best fit for CCl_4 is shown in figure 3 including the residual functions from the earlier fit [1] and from that with the modified Q-scale; the optimum χ^2-value is reduced by almost 50 per cent. The other data show a similar general behaviour but do not result in such large χ^2-reductions (table 2); the situation for $GeCl_4$ is shown in figure 2 (*c*). In all cases the bond length parameter r_{XCl} is unaltered as the statistical weighting function is primarily peaked in the 10 Å^{-1} region which remains unchanged. The conclusions presented earlier [1] about the evaluation of bond length values therefore are maintained and the sensitivity of the fitting procedure is improved. Anharmonicity effects may still be present but cannot be closely studied until a more complete characterization of the Q-scale calibration is obtained. It is interesting to compare these findings with the observations of Windsor and Cole [13] in the analysis of nickel powder patterns at high Q-values. These measurements were made on the backward scattering spectrometer (BSS) [14] which views the same moderator as that used in the current experiments. The peak profile for the Bragg peaks gives information on the pulse width and the positions of peaks arising from high order reflections from

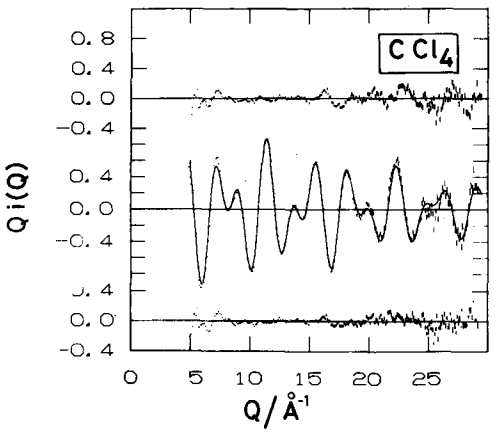

Figure 3. The effect of neutron mean emission time (equation (3.3)) on the $f_1(Q)$ fit for liquid CCl_4 [1] at 150° ; the final fit is shown to the $Qi(Q)$ data with the residual functions before (top) and after (bottom) inclusion of the correction.

parallel planes give an accurate measurement of the variation in mean emission time. The corresponding value of k_T for the powder data was 8 μs Å^{-1} [15] which is in remarkable agreement with the present findings, considering that the experiments were conducted on different instruments and concern total scattering and elastic scattering measurements respectively. This adds confidence to the methods currently adopted for the corrections and suggests that a more extended study of $\tau(\lambda)$ will be desirable to establish a detailed procedure for routine application to all diffraction measurements.

A full list of the bond lengths is given in table 3 and compared with other data. The agreement is very good even though molecular recoil corrections have not been applied to the data. This surprising result reinforces the conclusions obtained in the earlier paper [1] and emphasizes the need to obtain a correct formulation of the neutron scattering process for molecular systems in the condensed phase. The inelasticity effects of molecular vibration and recoil in the scattering process have been considered theoretically by Powles in a series of papers [16] on neutron scattering from isolated molecules in the gas phase. For the tetrachloride liquids studied in these experiments the predictions are not in very good agreement with the observations but the situation appears to be much better for other liquids such as nitrogen [17] and carbon disulphide [18]. Further analysis of different molecular systems should help to establish the current limitations of the Powles method and establish analytic expressions for the variation of the self-scattering contributions to the cross-section ; this work is proceeding and will be reported later. With the construction of facilities providing much higher neutron fluxes, the limitations to the accuracy of the final information will depend increasingly on an understanding of the systematic effects arising in the diffraction observations.

We wish to thank the staff of the Harwell Electron Linac, particularly Dr. Roger Sinclair, for assistance during the course of the experiments and Dr. Colin Windsor for discussions concerning the mean emission time corrections.

Professor Jack Powles has provided theoretical information and predictions of inelasticity corrections for some tetrachloride molecules prior to publication. Several of us wish to thank various organizations for financial support, i.e. the Science Research Council (GWS and JHC), the Atomic Energy Research Establishment (JHC), the Rotary International Foundation (JRG) and the International Atomic Energy Agency (JRG). The work was conducted with the support of the Neutron Beams Research Committee of the Science Research Council.

References

[1] Clarke, J. H., Granada, J. R., and Dore, J. C., 1979, *Molec. Phys.*, **37**, 1263.
[2] Gibson, I. P., and Dore, J. C., 1979, *Molec. Phys.*, **37**, 1281.
[3] Clarke, J. H., 1975, *Linac Neutron Diffraction Analysis Program*, LINDA, A.E.R.E. Report R-8121.
[4] Morino, Y., Nakamura, Y., and Iijlma, T., 1960, *J. chem. Phys.*, **32**, 643.
[5] Rutledge, C. T., and Clayton, G. T., 1975, *J. chem. Phys.*, **63**, 2211.
[6] Morino, Y., and Uehara, H., 1966, *J. chem. Phys.*, **45**, 4543.
[7] van Tricht, J. B., 1977, *J. chem. Phys.*, **66**, 85.
[8] Morino, Y., and Murata, Y., 1965, *Bull. chem. Soc. Japan*, **38**, 104.
[9] Rutledge, C. T., and Clayton, G. T., 1970, *J. chem. Phys.*, **52**, 1927.
[10] Fujii, H., and Kimura, M., 1970, *Bull. chem. Soc. Japan*, **43**, 1933.
[11] Carpenter, J. M., 1977, *Nucl. Instrum. and Meth.*, **145**, 91.
[12] Johnson, P. A. V., Wright, A. C., and Sinclair, R. N., 1978, A.E.R.E. Report R-8925.
[13] Windsor, C. G., and Cole, I., 1978 (unpublished report).
[14] Windsor, C. G., and Sinclair, R. N., 1976, *Acta crystallogr.* A, **32**, 395.
[15] Windsor, C. G. (private communication).
[16] Powles, J. G., 1978, *Molec. Phys.* **36**, 1161, 1181.
[17] Clarke, J. H., and Dore, J. C. (unpublished data).
[18] Gibson, I. P., Clarke, J. H., and Dore, J. C. (unpublished data).