Neutron Diffraction Study of Liquid Acetyl Chloride

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The structure factor $S_m(Q)$ for liquid acetyl chloride at room temperature has been determined in the range Q, 0.9—27 Å^{-1}, by means of the time-of-flight (TOF) neutron diffraction method using the electron linear accelerator (LINAC). The structural parameters of CD_3COCl, bond distances, bond angles, and rms amplitudes, in liquid phase have been determined by a comparison of calculated curves with observed data, and it has been concluded that a molecule within the liquid takes an essentially identical conformation as a rotational isomer with that in gaseous phase, which was determined by microwave spectroscopy.

Studies on neutron diffraction have been extensively carried out during the last three decades. Neutron diffraction as well as X-ray and electron diffraction has turned out to be a powerful means for determining the structure of condensed matter directly.[1] The method has been applied to structural studies of molecular liquids recently. The positions of light atoms as hydrogen (deuterium) contained in the molecules of organic liquids can be determined. A typical molecular liquid as an object of studies by means of neutron diffraction is heavy water. Studies were carried out by Page and Powles,[2] Narten,[3] and the authors.[4,5]

Neutron diffraction studies on molecular liquids including water have provided useful information. Dore *et al.* studied diatomic liquids (N_2, O_2, and Br_2) and other non-hydrogenous and heteronuclear molecular liquids (C_2O_3, $VOCl_3$, and XCl_4: X=C, V, Si, Ti, Ge, and Sn). Structure factors $S_m(Q)$ for a wide range of momentum transfer Q were determined for these materials.[6] Bertagnolli *et al.* carried out measurements for hydrogenous molecular liquids (CD_3CN and $CDCl_3$) and determined $S_m(Q)$ in the range of low Q.[7] In order to determine the structure and conformation of molecules in liquids, it is necessary to obtain the $S_m(Q)$ data in a wide range of Q values. The neutron diffraction experiment by LINAC is extremely useful for obtaining data for higher Q values.

The result of a neutron diffraction study on liquid acetyl chloride is given in the present paper. Studies were carried out on the molecular structure of acetyl chloride in gaseous phase with use of electron diffraction and microwave spectroscopy,[8-10] Sinnott's[9] result by microwave spectroscopy being considered to be accurate. However, the structure and configuration of the molecule in liquid state have never been studied. Conformation of the molecule within the liquid is of interest in comparison with that in gaseous phase as considered from the viewpoint that strong molecular interactions within liquid may cause a change of conformation as a rotational isomer. The authors have been able to obtain the $S_m(Q)$ for a wide range of Q which is sufficient to make a precise determination of the structure of the molecule within the liquid.

Experimental

Procedure for Measurements. The experiment was performed by means of the TOF neutron diffraction method by LINAC.[4,5] Details of the apparatus and procedure were reported.[4,11]

Deuterated acetyl chloride CD_3COCl (purity of deuteration 99%, Stohler Isotope Chemicals (USA)) was used. The coherent scattering amplitude, scattering cross sections, and the absorption cross section for each atom are given in Table 1. The effect of strong absorption by chloride nuclei at lower Q can be corrected easily since the atoms absorb neutrons according to the $1/v$ law in the low energy region (v: neutron velocity).

Table 1. Coherent scattering amplitude (b_{coh}), scattering cross sections (σ_{coh} and σ_{inc}) and absorption cross section (σ_a)[a]

Element	b_{coh} (fermis)	σ_{coh} (barns)	σ_{inc} (barns)	σ_a (barns)
D	6.67	5.59	2.0	0.00046
C	6.65	5.56	0	0.0033
O	5.80	4.23	0	<0.002
Cl	9.6	11.58	3.5	33.6
V	−0.4	0.02	4.9	4.98

$\sigma_{coh}=4\pi b_{coh}^2$ and $\sigma_{inc}=4\pi b_{inc}^2$, where b_{inc} is the incoherent scattering amplitude. a) B. Dorner and R. Comès, "Dynamics of Solids and Liquids by Neutron Scattering," ed by S. W. Lovesey and T. Springer, Springer-Verlag, Berlin (1977), Chap. 3, pp. 136—141.

Measurements were carried out at room temperature (16 °C) at two different scattering angles (2θ=45° and 150°). Time-of-flight of neutrons was analyzed with a multi-channel time analyzer with channel widths of 20 μs and 10 μs at the scattering angles of 45° and 150°, respectively. Thin-walled cyrindrical quartz vessels were used to contain samples.

We obtained the $S_m(Q)$ data for low Q region (Q=0.95—14 Å^{-1}) and those for a higher Q region (Q=3.0—27 Å^{-1}) by measurement at each scattering angle. The count rate time-spectrum is given in Fig. 1 together with smoothed spectra for vanadium and background normalized in burst number of LINAC.

Corrections and Calibrations of Raw Scattering Data.[2,4] In order to determine structure factors, corrections for multiple scattering, absorption, background counting, and inelastic scattering are necessary. Absolute normalization of data was performed with use of scattering data from a standard vanadium rod of the same shape and dimensions as the sample.[4] $S_m(Q)$ data obtained after the correction except for inelastic scattering are given in Fig. 2.

A steady fall in $S_m(Q)$ values, caused by the inelastic scattering of neutrons by light nuclei, is observed at higher Q. For compensating of the effect, several conventional and useful

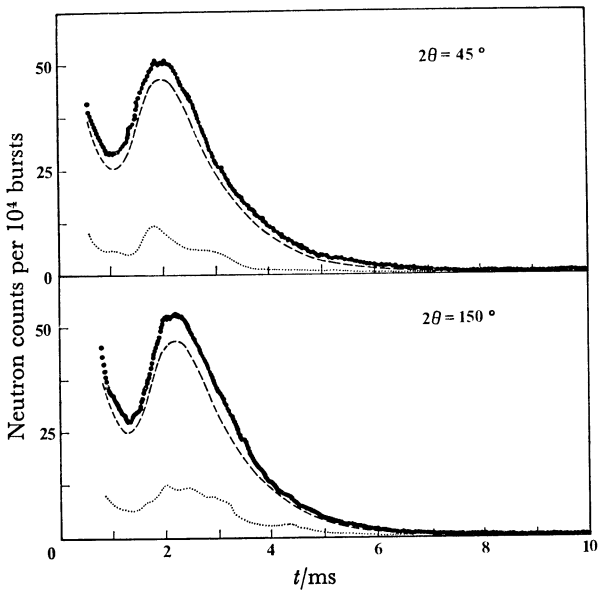

Fig. 1. Time-of-flight spectra.
●: CD_3COCl (16°C)+background, ------: vanadium +background, ·····: background.

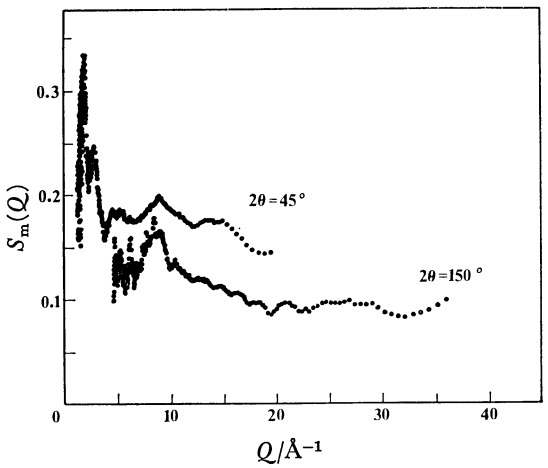

Fig. 2. The observed structure factor obtained after the application of corrections except that for inelastic scattering.

correction methods can be used. In the present study the Placzek method[12] was applied in a lower Q region and a dynamical correction method[13] in a higher Q region.

Calibration of absolute values for high Q data was performed considering the fact that $S_m(Q) \rightarrow \sum b_n^2/(\sum b_n)^2$ as $Q \rightarrow \infty$, where n ranges over all the nuclei in a molecule. Calibration for low Q data was made by overlapping the $S_m(Q)$ curves in the range 8—10 Å^{-1} for the two data sets. Thus, combining the two data sets,[6] we have obtained the final $S_m(Q)$ curve for the range of Q, 0.9—27 Å^{-1} (Fig. 3). The magnitudes of resolution ΔQ are given as triangles along the abscissa.[4] The statistical error was found to be smaller than 2.5% in the whole range of Q.

Results and Discussion

Analysis of Experimental Data. The structure factor $S_m(Q)$ for molecular liquids consists of an intra-

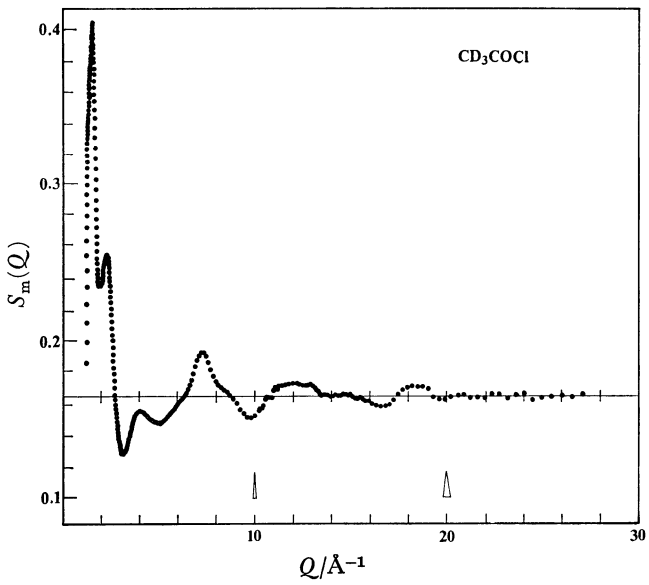

Fig. 3. The final structure factor $S_m(Q)$.
The magnitudes of the instrumental resolution are indicated by triangles at two points.

molecular structure factor $S_m^{(1)}(Q)$ and an intermolecular one $S_m^{(2)}(Q)$:

$$S_m(Q) = S_m^{(1)}(Q) + S_m^{(2)}(Q). \quad (1)$$

The higher the Q values, the smaller the $S_m^{(2)}(Q)$. Accordingly, structure factors for a higher Q region are characteristic of a single molecule, *viz.* the intramolecular structure factor

$$S_m(Q) \rightarrow S_m^{(1)}(Q) \text{ for high } Q. \quad (2)$$

For acetyl chloride the intramolecular structure factor becomes

$$S_m^{(1)}(Q) = (3b_D+2b_C+b_O+b_{Cl})^{-2}[3b_D^2+2b_C^2+b_O^2+b_{Cl}^2 + \sum_{i \neq j} b_i b_j j_0(Qr_{ij}) \exp(-\gamma_{ij}Q^2)], \quad (3)$$

where b_D, b_C, b_O, and b_{Cl} denote the coherent neutron scattering length of deuterium, carbon, oxygen, and chloride nucleous, respectively, $j_0(Qr)$ is a spherical Bessel function of zeroth order, and $(2\gamma_{ij})^{1/2}$ the rms amplitude to a bond length r_{ij}. The summation involved fifteen independent terms corresponding to different bond lengths.

The molecular model of acetyl chloride is shown in Fig. 4. The structure of the molecule except the methyl group is assumed to be a plane configuration,[9,10] and deuterium atoms in the methyl group are considered to

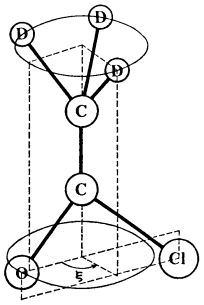

Fig. 4. The molecular model of acetyl chloride.

rotate about the C–C axis. At the rotational angle $\xi=0°$, a methyl deuterium atom eclipses oxygen atom (Fig. 4).

The structure of the molecule is characterized by the magnitudes of structural parameters: four bond lengths ($r_{C=O}$, r_{C-C}, r_{C-Cl}, and r_{C-D}), four rms amplitudes ($(2\gamma_{C=O})^{1/2}$, $(2\gamma_{C-C})^{1/2}$, $(2\gamma_{C-Cl})^{1/2}$, and $(2\gamma_{C-D})^{1/2}$), four bonding angles ($\angle$C–C=O, $\angle$C–C–Cl, $\angle$D–C–C, and $\angle$D–C–D), and a rotational angle ξ (Fig. 4). Values of these parameters determined so far for gas molecules of CH_3COCl by means of electron diffraction and microwave spectroscopy are summarized in Table 2,[8–10,14,15] the rms amplitudes being cited from the results of electron diffraction studies of formic acid (C=O)[14] and of *n*-propyl chloride (C–C, C–Cl, and C–H).[15]

Table 2. Molecular parameters determined by electron diffraction (ED) and microwave (MW) methods

	ED[8]	MW[9]	$(2\gamma_{ij})^{1/2}$ [15]
Bond length (Å)			
C=O	1.22±0.04	1.192±0.010	<0.030[14]
C–C	1.50±0.04	1.499±0.010	0.036
C–Cl	1.77±0.02	1.789±0.005	0.051
C–H	1.09(assumed)	1.083±0.005	0.067
Bond angle			
$\angle$C–C=O		127°5′±10′	
$\angle$C–C–Cl	110°±3°	112°39′±30′	
$\angle$H–C–H		108°44′±30′ [a]	
$\angle$H–C–C	109.5°	110°21′±10′	

a) L. C. Krisher and E. B. Wilson, Jr., *J. Chem. Phys.*, **31**, 882 (1959).

Determination of the Intramolecular Structure within Liquid. In order to determine the molecular parameters and investigate the internal rotation of the methyl group by means of Eq. 2, $S_m^{(1)}(Q)$ was calculated for a number of structure models using Eq. 3, the magnitudes of the parameters being varied in reference to the values given in Table 2. The procedure of analysis is as follows.

Firstly, $S_m^{(1)}(Q)$ values were calculated with a variation of ξ successively at intervals of 10° from 0° to 80° and also for the averaged values corresponding to the free rotation of the methyl group about the C–C axis.[2,4] The parameters involving deuterium atom only (r_{C-D}, $\angle$D–C–D, and $\angle$D–C–C) were varied as follows: r_{C-D}, 1.085—1.105 Å at 0.005 Å step, $\angle$D–C–D, 108.5±1.0° and $\angle$D–C–C, 110.5±1.0°. The remainder of parameters were fixed to the values in Table 2. At the first stage we calculated the $S_m^{(1)}(Q)$ for 495 models. A typical example of the $S_m^{(1)}(Q)$ curves calculated with the variation of ξ is shown in Fig. 5. The best fit curve at the first stage of analysis with the experimental data is obtained at $\xi=0°$, $r_{C-D}=1.095$ Å, $\angle$D–C–D=108.5° and $\angle$D–C–C=110.0°.

Secondly, in order to determine more precisely the eight parameters (r_{C-C}, $r_{C=O}$, r_{C-Cl}, r_{C-D}, $\angle$C–C=O, $\angle$C–C–Cl, $\angle$D–C–D, and $\angle$D–C–C), keeping the value of ξ at 0° and fixing the values of rms amplitudes to the values in Table 2, we calculated $S_m^{(1)}(Q)$ for 435 models, the parameters being varied in the range given

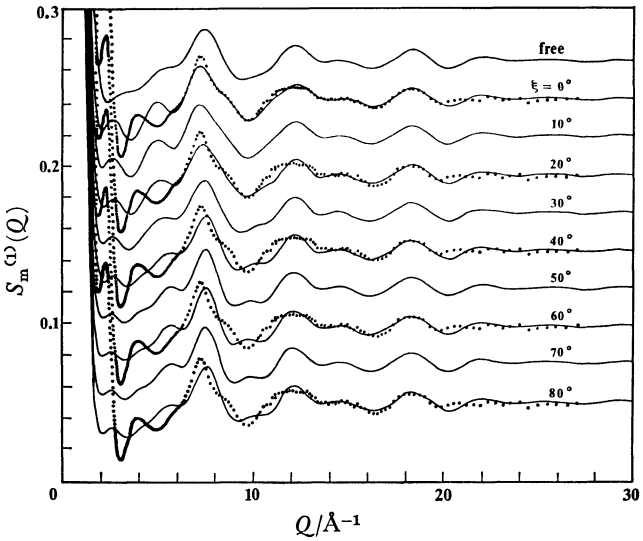

Fig. 5. The calculated $S_m^{(1)}(Q)$ with the variation of rotational angle ξ.
●: $S_m(Q)$ observed, ——: $S_m^{(1)}(Q)$ calculated.

Table 3. Range of parameters

Parameter	Range	Interval of variation
	(Å)	(Å)
$r_{C=O}$	1.400—1.600	0.005
r_{C-C}	1.175—1.205	0.005
r_{C-Cl}	1.775—1.805	0.005
r_{C-D}	1.085—1.105	0.005
	(degree)	(degree)
$\angle$C–C=O	125.0—129.0	1.0
$\angle$C–C–Cl	110.5—113.5	1.0
$\angle$D–C–D	107.5—109.5	0.5
$\angle$D–C–C	109.5—111.5	0.5

Table 4. Molecular parameters determined by neutron diffraction method

	r_{ij} (Å)	$(2\gamma_{ij})^{1/2}$ (Å)		Bond angle (degree)
C=O	1.190±0.010	0.029	$\angle$C–C=O	127.0±1.0
C–C	1.500±0.005	0.036	$\angle$C–C–Cl	112.5±1.0
C–Cl	1.790±0.010	0.052	$\angle$D–C–D	108.5±0.5
C–D	1.095±0.005	0.066	$\angle$D–C–C	110.0±0.5

in Table 3. From a comparison of the calculated curves with experimental result, the parameters (except rms amplitudes) which gave the best fit model were determined (Table 4).

Finally, for the case of the parameter set thus determined calculations for 32 models with the variation of the rms amplitudes were carried out and the curves obtained compared with experimental results. The magnitudes of the rms amplitudes are also given in Table 4. The best fit curve with the experimental data is shown in Fig. 6. Agreement of both curves is excellent in the range of Q values, 5.5—20 Å^{-1}. The apparent deviations beyond $Q\gtrsim20$ Å^{-1} are insignificant and negligible. The deviation of the calculated $S_m^{(1)}(Q)$

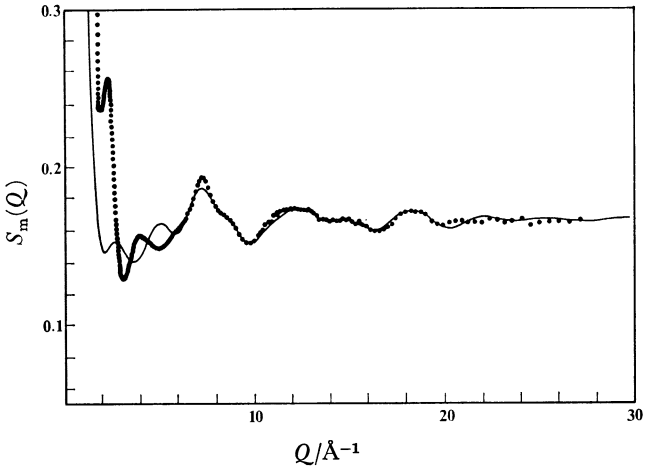

Fig. 6. Comparison of the calculated $S_m^{(1)}(Q)$ with the observed $S_m(Q)$.
●: $S_m(Q)$ observed, ——: $S_m^{(1)}(Q)$ calculated for the best model.

from the experimental curve in low Q region ($Q \lesssim 5.5$ Å^{-1}) is ascribed to the intermolecular contribution in liquid not included in the calculation (Eq. 3).

The results show that one methyl deuterium atom eclipses oxygen atom for the molecule in liquid as well as in gaseous phase. The molecular parameters assigned for liquid acetyl chloride (Table 4) are nearly identical with those determined for the molecule in gaseous phase by Sinnott.[9] The C–D bond length ($=1.095 \pm 0.005$ Å) is slightly larger than those in methyl groups.[9]

Conformation of a Molecule in Liquid Acetyl Chloride in Comparison with That in Gaseous Phase. A molecule within a system often changes its conformation through a phase transition. A typical example is the case of 1,2-dichloroethane ($C_2H_4Cl_2$) which has been studied fairly in detail.[16,17] A $C_2H_4Cl_2$ molecule in solid phase takes trans-conformation only; in liquid phase trans- and gauche-molecules are present at a ratio of *ca.* 1: 1.92 in number; in gaseous phase the fraction of gauche-molecules decreases.

A molecule in gaseous phase seems to change its conformation as a rotational isomer in liquid and solid phase, as considered from the stronger effects of molecular interactions in condensed phases. According to the present result the situation for CD_3COCl differs from that for $C_2H_4Cl_2$. We have confirmed that all the CD_3COCl molecules in liquid phase take the conformation in which a deuterium atom in CD_3 group of the molecule eclipses the oxygen atom like that in gaseous phase.[18] A CD_3COCl molecule as a rotational isomer about the C–C axis does not change its conformation essentially through a phase change from gaseous to liquid state, the conformation being kept as shown in Fig. 4.

Microwave spectroscopy and electron diffraction have been used widely for determination of the structure of molecules, but application of the methods is mostly confined to gaseous systems. For determination of the molecular conformation within liquid, the neutron diffraction technique is considered important when used in combination with other techniques applicable to gases.

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