

The Local Structure of Liquid TiCl_4 Analyzed by X-Ray Diffraction and Raman Spectroscopy

Yasuhiko Iwadate and Takahiro Ohkubo

Department of Applied Chemistry and Biotechnology, Graduate School of Engineering,
Chiba University 1-33, Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

Reprint requests to Y. I.; E-mail: iwadate@faculty.chiba-u.jp

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Dedicated to Professor Alfred Klemm on the occasion of his 100th birthday

Structural analyses were performed to determine the local structure of liquid TiCl_4 using laboratory-scale X-ray diffraction and Raman spectroscopy from which the existence of tetrahedral TiCl_4 molecules in the liquid was definitely confirmed. Conventionally, in molten salts, the valence increase of the central metal ion, for example in the range from 1 to 3, leads to more complicated liquid structures, yet a further increase in valence is usually accompanied by an enhanced covalency, forming stable tetrahedral molecules like e. g. CCl_4 . We discuss the intermolecular structure of TiCl_4 liquid as well as the intramolecular one.

Key words: Local Structure; TiCl_4 ; Tetrahedron; XRD; Raman.

1. Introduction

The term ‘molten salts’ has long been used to express ‘melts of inorganic compounds’ composed of cations and anions. Molten salts have been classified into high temperature ionic melts in the narrow sense when the ionic liquids at ambient temperatures appeared; these are relatively bulky, but ionic organic solvents. As time goes by, however, the definitions of both liquids tend to overlap. The physicochemical properties of molten salts have certainly a close relation to the structures of liquids assumed to be composed, at high temperatures, of mobile cations and anions. It is thus of much importance to acquire structural information for a systematic understanding of these properties.

X-ray diffraction (XRD) [1–8] and neutron diffraction (ND) [9–11] have mostly been employed to analyze the structure of molten salts. In order to understand the liquid structure quantitatively, the radial distribution function $D(r)$ (RDF) and/or the correlation function $G(r)$ of a given constituent ionic pair have to be estimated from diffraction work. The coordination numbers of individual atomic pairs can be estimated from the deconvolution of $D(r)$ into respective peaks and by integration of each contribution up to an interatomic distance r . These analytical procedures are carried out in real space. For the analyses in reciprocal lat-

tice space, the trials of Narten et al. [12–14] based on the Debye scattering equation as well as the algorithm proposed by Busing and Levy [15] are of great advantage and service. Another experimental technique is Raman spectroscopy [16, 17], providing vibrational modes of chemical species in the melts such as complex ions, clustered species, and molecules.

The structure of several CCl_4 -type liquids have so far been reported [18–21], and in particular Nath et al. [21] have pointed out that the intermolecular structure and correlation of tetrachloride liquids including GeCl_4 and VCl_4 can be well described by Misawa’s orientation correlation model originally applied to liquid CCl_4 [19].

In the present work, the short-range structure of liquid TiCl_4 as a typical tetravalent compound like CCl_4 was analyzed by XRD and Raman. The result was compared with those previously reported, and finally the structural characteristics of TiCl_4 liquid are discussed.

2. Experimental

2.1. TiCl_4 Sample

High purity grade TiCl_4 (>99.9%) was supplied by Toho Titanium Co., Ltd., the main metallic impurities such as Si, Fe, V, Cu, Sn, Nb, Mn, Ni, Cr, and

Al were checked to be less than 2 ppm in all cases. The as-prepared sample was introduced into a semi-cylindrical cell made of thin quartz and sealed during ice-cooling under reduced pressure in order to prevent the sample from reacting with moisture, since the active chemical reaction of TiCl₄ with H₂O produces strong hydrolysis with large heat of reaction.

2.2. Raman Spectroscopy

The liquid sample was introduced into a transparent cylindrical fused silica cell of 4 mm in inner diameter, 6 mm in outer diameter, and 130 mm in height in the glove box and sealed under reduced pressure. Raman spectra were measured at room temperature with a specially redesigned Raman spectrophotometer (original apparatus: NR-1800, JASCO, Japan) equipped with a triple monochromator using an Ar⁺ ion laser at the wavelength of 514.5 nm with an output of 600 mW as an excitation light source. The data acquisitions were made 5 times in the wavenumber range from 10 to 700 cm⁻¹ with a sampling step of 0.1 cm⁻¹ and a scanning speed of 6 cm⁻¹min⁻¹ to smooth the spectra of simply scattered light, of light scattered parallel (*I_{VV}*) and perpendicular (*I_{HV}*) to the polarization of the incident light. The Raman cell and the sample holder assembly are sketched elsewhere [22].

2.3. X-Ray Diffraction

Prior to XRD, the molar volumes were estimated from the density data measured at several temperatures and expressed as a least squares fitted function of temperature in the form (*V_m*/cm³mol⁻¹) = 0.11755(*T*/K) + 75.4032.

According to this empirical equation, the molar volume at ambient temperature was calculated so as to evaluate the atomic number density of the liquid, 0.0054647 Å⁻³.

In the X-ray scattering measurements, an X-ray diffractometer having a θ - θ type reflection geometry (Rigaku Corporation, Tokyo, Japan) was employed with MoK α radiation, and the diffracted beam was monochromatized with curved graphite. The *S*-range, 0.93 ≤ *S*/Å⁻¹ ≤ 12.5, was explored with two pairs of divergence and scattering slits [1/2°–1/2°] when 2.5° ≤ θ ≤ 15°, and [1°–1°] when 13° ≤ θ ≤ 45° (2 θ = scattering angle and *S* = 4 π sin θ /λ with λ being the wavelength of the radiation 0.71069 Å; 1 Å =

10⁻¹⁰ m). The receiving slit was 0.6 mm throughout this work. The scattered X-ray intensities so obtained at ambient temperature were corrected for background, polarization, absorption, and Compton scattering, and normalized to the coherent scattering intensity of the stoichiometric unit, in accordance with the usual procedure [23]. Atomic scattering factors and Compton scattering factors were taken from the literature [24, 25]. Thus, the experimental structure factors and radial distribution functions were obtained.

3. Results and Discussion

3.1. Vibrational Modes of TiCl₄ Liquid

The vibrational features of the TiCl₄ liquid were studied by Raman spectroscopy in order to specify the chemical species existing in the medium. The structure of conventional molten salts as well as the valence effect of a centered element on the structure of clustered species and molecules are then briefly outlined and discussed.

Since the Raman spectrum of liquid TiCl₄ included a background due to the Rayleigh wing, which reaches the high wavenumber region, the background (BG) was approximated as a sum of Gaussian and Lorentzian functions by using a least squares fit as

$$\text{BG} = A \cdot \exp \left[- \left\{ (v - v') / B \right\}^2 \right] + C / \left[1 + \left\{ (v - v') / D \right\}^2 \right]. \quad (1)$$

The fitted parameters of *A*, *B*, *C*, *D*, and the Rayleigh shift *v'* were calculated from the data in the range below 60 cm⁻¹ and above 650 cm⁻¹. Each Raman shift was determined so that the BG was subtracted from the observed spectrum and then the Raman components were approximated by a Lorentzian function,

$$I(v) = I(v_0) / \{ 1 + (v - v_0)^2 / w^2 \}, \quad (2)$$

where *v*, *v*₀, *I*(*v*), *I*(*v*₀), and *w* refer to a given wavenumber, a Raman shift, the intensity at a given *v*, the maximum Raman intensity at *v*₀, and the full width at half height of the maximum, respectively.

Moreover, the electrical resistivity of this medium was found to be very close to that of an insulator in preliminary measurements. The liquid was thus thought to be molecular rather than ionic. The Raman spectra were analyzed on the basis of this assumption. There

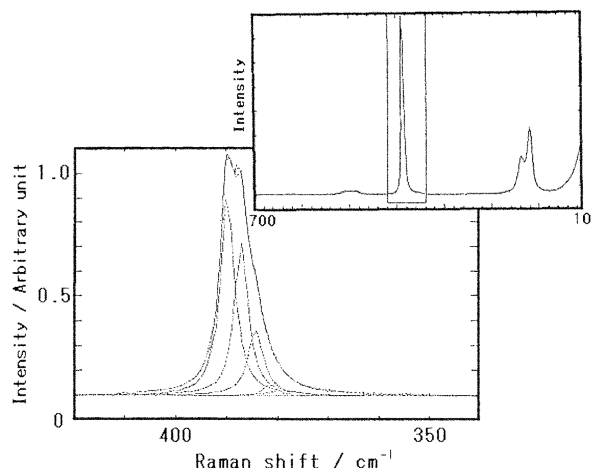


Fig. 1. Band profile analysis of the ν_1 mode in liquid TiCl_4 .

are conventionally four normal modes of vibration for tetrahedral configuration, all of which are Raman active. In the range from 50 to 200 cm^{-1} , two peaks were observed at 119.5 and 137.4 cm^{-1} , the intensities of which were not much reduced by changing the polarization characteristics of the incident laser beams. In the range of 340 to 420 cm^{-1} , a large peak was observed, whose degree of depolarization, $I_{\text{HV}}/I_{\text{VV}}$, was estimated to be less than 0.03 . This indicated that the large peak was assignable to a totally symmet-

Table 1. Numerical data of the Raman spectra of liquid TiCl_4 .

Mode	Raman shift / cm^{-1}	Peak height	Width / cm^{-1}
ν_1	378.9	1.76	3.10
	381.5	3.59	1.29
	384.2	19.70	1.79
	387.0	45.50	1.60
	389.7	60.90	1.62
ν_2	119.5	25.10	6.04
ν_3	490.0	—	—
ν_4	137.4	12.50	6.58

ric stretching vibration ν_1 . A more precise inspection of this ν_1 band enabled us to see the finer structure of the spectrum, that is, an asymmetry in the band shape, as shown in Figure 1. According to the numerical band profile analyses, the ν_1 band consists of five Raman component peaks centered at 378.7 , 381.5 , 384.2 , 387.0 , and 389.7 cm^{-1} .

In naturally abundant Cl, there are two stable isotopes, ^{35}Cl and ^{37}Cl , in atomic fractions of 75.53% and 24.47% , respectively. Accordingly, there are five kinds of isotope-substituted molecules such as $\text{Ti}^{35}\text{Cl}_4$, $\text{Ti}^{35}\text{Cl}_3^{37}\text{Cl}$, $\text{Ti}^{35}\text{Cl}_2^{37}\text{Cl}_2$, $\text{Ti}^{35}\text{Cl}^{37}\text{Cl}_3$, and $\text{Ti}^{37}\text{Cl}_4$. This change in mass brings about small, but measurable, variations in wavenumber. Clark et al. have reported the splitting of ν_1 band in solid TiCl_4 to be at 378.7 , 381.5 , 384.2 , 386.9 , and 389.7 cm^{-1} , these results corresponded very well to those reported above

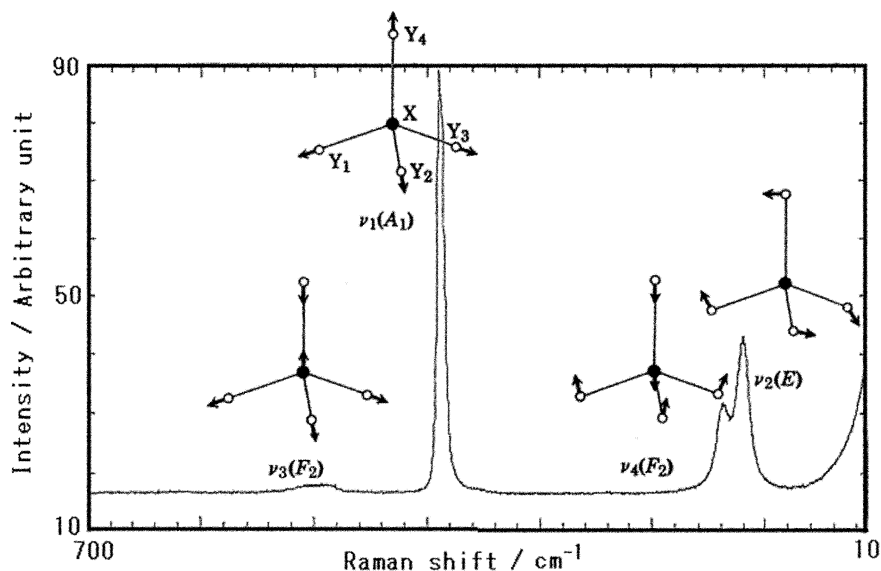


Fig. 2. Band assignment of the Raman spectra in liquid TiCl_4 .

for the liquid [26–28]. This proves that the TiCl₄ molecule remains stable even in the liquid.

An asymmetric broad band was observed in the vicinity of 500 cm⁻¹. This band was thought to be due to ν_3 , but further analysis was impossible on the grounds that its Raman intensity was too low even if Fermi resonance and similar effects were considered [29]. The final assignments of the Raman spectrum of XY₄-type tetrahedral TiCl₄ in the liquid are indicated in Figure 2, and the numerical results are listed in Table 1.

3.2. Local Structure of TiCl₄ Liquid

In terms of Raman spectroscopy, only individual TiCl₄ molecules are practically seen in the liquid, the intra- and intermolecular structure was thus studied by XRD. The reduced intensity function $S \cdot i(S)$, the radial distribution function $D(r)$, and the correlation function $G(r)$, are defined by

$$S \cdot i(S) = S \cdot \left[I_{eu}^{\text{coh}}(S) - \sum_i f_i(S)^2 \right] / \left(\sum_i f_i(S) \right)^2, \quad (3)$$

$$D(r) = 4\pi r^2 \rho_o + (2r/\pi) \int_0^{S_{\text{max}}} S \cdot i(S) \sin(Sr) dS, \quad (4)$$

$$G(r) = 1 + (2\pi^2 r \rho_o)^{-1} \times \int_0^{S_{\text{max}}} S \cdot i(S) \sin(Sr) dS, \quad (5)$$

where $I_{eu}^{\text{coh}}(S)$ is the total coherent intensity function and $f_i(S)$ the theoretical independent atomic scattering amplitude; summation is made over the stoichiometric units in a molecule; ρ_o is the number of stoichiometric units per unit volume and S_{max} the maximum value of S reached in the scattering experiment. Introduction of the term $(\sum_i f_i(S))^2$ into (3) makes the product $f_i(S)f_j(S)/(\sum_i f_i(S))$ in (6) nearly independent of S and thus removes from the resulting correlation function most of the average breadth of the distribution of electron density in the atoms:

$$\begin{aligned} i(S) &= \left[I_{eu}^{\text{coh}}(S) - \sum_i f_i(S)^2 \right] / \left(\sum_i f_i(S) \right)^2 \\ &= \left[\sum_i \sum_j f_i(S)f_j(S) / \left(\sum_i f_i(S) \right)^2 \right] \\ &\quad \cdot \int_0^\infty 4\pi r^2 [\rho_{ij}(r) - \rho_o] \sin(Sr) / (Sr) dr, \end{aligned} \quad (6)$$

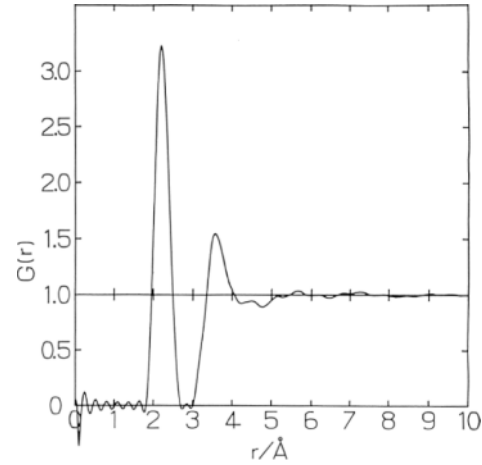


Fig. 3. Correlation function $G(r)$ of liquid TiCl₄.

where the function $i(S)$ is related to the radial density $4\pi r^2 \rho_{ij}(r)$ of distinct atoms pairs $i-j$. These analytical procedures are about the same as those of Narten [14].

As shown in Figure 3, two peaks, at about $r = 2.2$ and 3.6 Å, as well as a feeble peak at around 4.6 Å were observed in the $G(r)$ curve. Since the effective ionic radii of Ti⁴⁺ and Cl⁻ were estimated at 0.42 and 1.81 Å by Shannon [30], the first peak at 2.2 Å was thought to be assignable to Ti–Cl pairs. There was a steep-walled valley between the first and second peaks on the $G(r)$, and the first peak on the $D(r)/r$ curve had a very good symmetry. Accordingly, the interatomic pairs other than Ti–Cl were assumed to make no contribution to the first peak. Next, the nearest neighbour coordination number of Cl around Ti was calculated to be about 3.8 by integration of the first peak area on the $D(r)$ curve. The peaks near $r = 3.6$ and 4.6 Å could be roughly assigned to Cl–Cl and Ti–Ti pairs, respectively. The $D(r)/r$ and the $D(r)$ curves are illustrated in Figure 4.

In order to confirm the above assumptions, that is, to refine the short range structure of TiCl₄ liquid, the structural parameters for each ionic pair are necessary to be optimized by the correlation method, using the nonlinear least squares fit

$$\begin{aligned} S \cdot i(S) &= \left[\sum_i \sum_j n_{ij} f_i(S) f_j(S) \exp(-b_{ij} S^2) \right. \\ &\quad \cdot \sin(Sr_{ij}) / r_{ij} \left. \right] / \left(\sum_i f_i(S) \right)^2, \end{aligned} \quad (7)$$

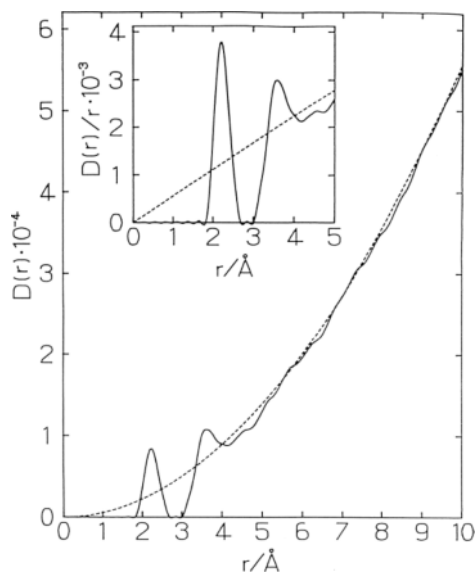


Fig. 4. Radial distribution function $D(r)$ and scaled function $D(r)/r$ of liquid TiCl₄.

where n_{ij} , r_{ij} , and b_{ij} refer to the average coordination number, the average interatomic distance, and the temperature factor for the ionic pair $i-j$, respectively. Each atomic pair was presumed to be Gaussian distributed, centered at r_{ij} with a mean square displacement $2b_{ij}$. For determining the validity of the model structure, the following parameter is often introduced, where R is the degree of coincidence in fitting of two interference functions:

$$R = \frac{\sum \{ |S \cdot i(S)_{\text{cal}} - S \cdot i(S)_{\text{obs}}| \}}{\sum \{ |S \cdot i(S)_{\text{obs}}| \}}. \quad (8)$$

The structural parameters obtained from $G(r)$ and $D(r)$ were used as the initial values of this process for their further refinement. Each parameter was optimized by a least squares regression beyond $S = 1.75 \text{ \AA}^{-1}$. The parameters of the most probable model in the $S \cdot i(S)$ fit are given in Table 2. The observed and calculated $S \cdot i(S)$'s of liquid TiCl₄ are shown in Figure 5. The R factor for the best fitted model of this liquid in intervals of 0.05 \AA^{-1} in the range of $1.75 \leq S/\text{\AA}^{-1} \leq 12.5$, converged to 0.158. From this result, the nearest neighbour distance was estimated to be 2.17 \AA , the coordination number of Cl around Ti was 3.8, the like-ion pair distances Cl–Cl was 3.58 \AA , and Ti–Ti was calculated to be 4.57 \AA . The ratio of $r(\text{Cl–Cl})/r(\text{Ti–Cl})$ was 1.65, being close to the value for tetrahedral geome-

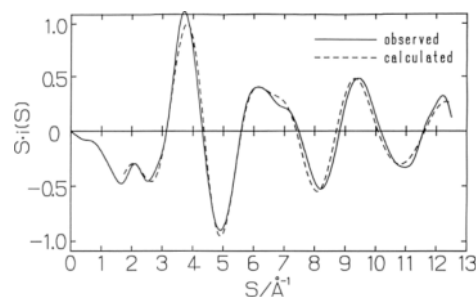


Fig. 5. Reduced intensity function $S \cdot i(S)$ of liquid TiCl₄. Both the intramolecular and the intermolecular correlations are considered in the estimations.

tries, 1.63. Especially, the intramolecular pair distances of Ti–Cl and Cl–Cl were in good agreement with the corresponding values of 2.16 \AA and 3.52 \AA in neutron diffraction experiment by van Tricht [18] and 2.17 \AA and 3.54 \AA in electron diffraction by Morino and Uehara [31], respectively. Similar results, $r(\text{Ti–Cl}) = 2.17 \text{ \AA}$ and $r(\text{Cl–Cl}) = 3.54 \text{ \AA}$, have recently been evaluated by neutron diffraction and reverse Monte Carlo (RMC) calculations [20].

The medium range structure, especially characterized by intermolecular structures such as Ti–Ti correlations, has been considered in terms of the molar volume and the obtained short range structural parameters. As mentioned, non-conductive TiCl₄ exists as a molecule in the pure liquid at ambient temperature and pressure. From the molar volume, if the TiCl₄ molecules were distributed isotropically, the average Ti–Ti pair-distance would be 5.68 \AA . The corresponding distance obtained from the X-ray diffraction analyses was 4.57 \AA . This indicates that, as for the Ti–Ti pairs, there are some specific configurations in the liquid, which would be well interpreted by a two-fold coordination at relatively short-range and some other coordinations, centered at about 5.7 \AA and widely distributed, reflecting the average number densities. It was, however, not possible to determine the contributions of the latter coordinations and the relative orien-

Table 2. Coordination number n_{ik} , interatomic distance r_{ik} , and root mean square displacement $\langle \Delta r_{ik}^2 \rangle^{1/2}$ for the intra- and intermolecular structure of liquid TiCl₄.

	$i-k$	n_{ik}	$r_{ik} / \text{\AA}$	$\langle \Delta r_{ik}^2 \rangle^{1/2} / \text{\AA}$
intramolecule	Ti–Cl	3.8	2.17	0.122
	Cl–Cl	2.9	3.58	0.213
intramolecule	Ti–Ti	2.1	4.57	0.467

tations of adjacent molecules from the contributions of the intermolecular Cl–Cl and Ti–Ti pairs because of the very small contribution in scattered X-ray intensity over low S region. It was described by van Tricht [18] that in the case of molecular liquids the diffraction pattern beyond a wave number transfer S of about 7 \AA^{-1} in ND (5 \AA^{-1} in the present XRD) is almost entirely due to intramolecular scattering.

Conventionally, monovalent melts were assumed to be dissociated into discrete ions, divalent and trivalent ones being labeled complex ions and/or molecules. However, the above findings indicate that there exist stable tetrahedral TiCl₄ molecules in pure liquid TiCl₄ at ambient temperature and pressure with formation of neither complex ions nor clustering. As mentioned before, an electronegative atom plays an important role in the intramolecular bonding between atoms. The differences in the electronegativities of two elements can be used to predict the nature of the chemical bond [32]. Bond types can be described as belonging to one of three classes: i) nonpolar covalent; ii) polar covalent; iii) ionic. When the difference in electronegativity is 1.7 or more, the bond is usually ionic; less than 1.7, the bond is usually covalent, and unless the difference is less than 0.5, the bond has some degree of polarity. Differences of less than 0.5 are considered to be nonpolar. In the case of TiCl₄, the electronegativities of Ti and Cl have been estimated at 1.54 and 3.16, respectively.

Based on the above criteria, the bond nature between Ti and Cl must be covalent. The covalency between the atoms of TiCl₄ is strong in comparison with the pairs of Cl and alkali metal or alkaline earth metal, which are typical pairs in ionic melts. The interactions between chemical species (molecules) are consequently very weak, providing less orientational ordering of the TiCl₄ molecules and making it difficult to estimate the coordination number of the intermolecular Ti–Ti correlations.

4. Conclusions

According to X-ray diffraction and Raman spectroscopy, the existence in the liquid at ambient conditions of tetrahedral TiCl₄ molecules without dissociation was confirmed. It was thus confirmed that the valence increase of a metal ion, or of a centered atom, (+1 to +3), leads to a more complicated liquid structure but that a further increase in valence (+3 to +4) leads to covalency-enhanced forms, i. e. to stable molecules.

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