



J. Serb. Chem. Soc. 86 (11) 1067–1074 (2021)
JSCS–5483

IR detection of the methane halides fluid-like state at ambient conditions

IOSIF GRINWALD* and ROSTISLAV KAPUSTIN

*Nizhny Novgorod State Technical University n.a. R.E. Alekseev Minin str. 24,
603950 Nizhniy Novgorod, Russia*

(Received 26 April, revised 24 June, accepted 28 June 2021)

Abstract: The paper presents the IR-study of the fluid-like state, generated at ambient conditions, for methane halides (iodomethane, tetrachloromethane, trichloromethane and dichloromethane). It was shown that at vapor compression-extension procedure realized in variable thickness spectral cell (VTOC), the dual phase state exhibiting both gas and liquid properties arises. A reversible transition from a gas-like to a liquid-like shape, independent on the thermodynamic characteristics of the studied methane halides, was revealed.

Keywords: dual phase state; phases transition.

INTRODUCTION

Fluid is a unique phase state of matter generating under supercritical conditions and combining the properties of gas and liquid. It is conventional to divide fluid state into gas-like and liquid-like shapes, depending on which properties prevail in them. However, this definition is ambiguous due to the continuous nature of the transition between these two states.^{1,2}

Supercritical fluids have many applications in industry, largely due to their tunable density, for example, they are used as environmentally friendly solvents for hazardous waste cleanup. However, the same properties that make fluids useful also make their generation quite difficult. Besides the high pressures and temperatures required, chemically active fluids can corrode many components of the experimental apparatus. Therefore, the formation of supercritical fluids is generally limited to the simplest compounds – water and carbon dioxide.^{3,4}

One of the most perspective methods of fluid study seems to be IR-spectroscopy since it clearly shows the transition of gaseous properties to liquid ones, with all accompanying transformations. However, IR study of fluids behavior and their liquid-like to gas-like state transitions are presented only in a few works

* Corresponding author. E-mail: grinwald@mts-nn.ru
<https://doi.org/10.2298/JSC210426048G>



to date.^{5,6} Nevertheless, what has already been published is thought-provoking. For example, in supercritical water the broad band of stretching O–H vibrations typical for liquid water or the bands with rotational structure of gaseous state are not observed at all. Instead, the P-, Q-, R-branches appear (for dilute gas-like fluid state) and then transform into non-broadened bands (for dense liquid-like fluid state).⁷

This effect is similar to the transformation in IR spectra of some organic species at liquid–gas transition observed at ambient conditions.⁷ For example, in the gas phase spectrum of benzene the band of C–H bond out-of-plane bending vibrations has the P-, Q-, R-branches. In the spectrum recorded for liquid benzene in thin layer between optical windows three unresolved components resembling the mentioned branches are observed.⁸ The gaseous spectrum of iodomethane manifests two band shapes for each vibration with the C–H bond participation. The first of them has a gas-like rotational structure, and the second one has a single counter like in liquid.⁸ The analogous picture was revealed for the C–Cl stretching in the gaseous spectrum of tetrachloromethane.⁹

The presented data indicate on the fact that the organic substances can demonstrate, at ambient conditions, a combination of gas and liquid properties. Therefore, it was reasonable to formulate the aim of this work, to generate at ambient conditions and to study by IR method the phase state that has fluid features, which could be defined by the term “fluid-like state”. According to this problem we have obtained and analyzed IR spectral data relating to fluid-like state of iodomethane, tetrachloromethane, trichloromethane and dichloromethane.

EXPERIMENTAL

For the fluid-like phase generation, the variable thickness IR optical cell was applied (here we use the abbreviation VTOC). In Fig. 1 the projection on the left side shows the optical design of the cell, and the projection on the right side shows the design for controlling the thickness of the cell. The cotton balls, soaked in liquid, were put inside two stainless steel

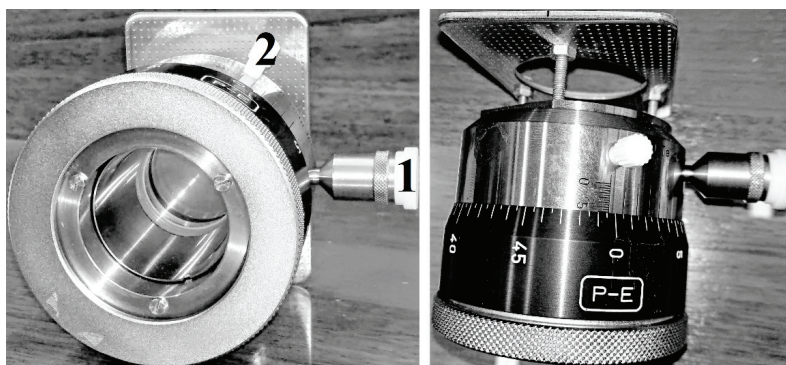


Fig. 1. The VTOC for the fluid-like state generation and detection. 1 – stainless steel funnel; 2 – Luer plug.

funnels with the plastic lids (Fig.1, (1)) to initiate the evaporation process. After the vapor inside the cell reached the required concentration, which was monitored by IR spectroscopy, the funnels were replaced with the Luer plugs (Fig.1, (2)).

The formation of the dual gas-liquid state occurred under the compression-extension procedure of the cell inter-window distance from 6 to 1 mm and in reverse. The optimal evaporation time required for the fluid-like state formation highly depends on the compound type and varies from 2 to 70 h. Experimental data for the selected samples is listed in the Table I, as well as their boiling temperatures.¹⁰ For the spectral detection of the generated state, IR spectra recorded in VTOC were compared with those obtained in a gas cell (for gas phase) and between optical KBr windows (for liquid state) at 23 °C.

TABLE I. The optimal time for the fluid-like state formation and the boiling point of the selected compounds

Parameter	CH ₃ I	CCl ₄	CHCl ₃	CH ₂ Cl ₂
t / h	70	2	12	26
T / °C	42.5	76.7	71.3	39.8

IR-spectra were recorded by IR-Fourier spectrometer FSM 1202 (InfraSpec Co.) in 4000–500 cm⁻¹ range with 2 cm⁻¹ resolution by 60 scans. The spectra fragments in the figures are given with the wavenumber's axis extension accordingly to original recording of the spectral device. The VTOC used with KBr windows was manufactured by Perkin-Elmer Co. The purity of halides was not less than 99 % as it was confirmed by chromat-mass spectrometry data obtained by GCMS-QP2010 Plus spectrometer (Shimadzu Co. Inc.).

RESULTS AND DISCUSSION

Iodomethane

In the spectrum region of iodomethane bending (H–C–H) vibrations, recorded at 6 mm thickness (Fig. 2, spectrum 1), the gas-like phase bands at 1263, 1241 cm⁻¹ (Fig. 2, band A, B) as well as a broad band with rotational structure at 1426 cm⁻¹ (Fig. 2, band C), were observed. Since the IR spectra of regular gases cannot be observed at such distance between optical windows, the appearance of two band types, with rotational structure and without it, corresponding to the same vibration, can occur owing to the formation of two differently built systems in gas-like state. Taking this conception, the band with the rotational structure assigns to bonded molecules with flatter geometry of (CH₃)-fragment, arising due to the iodine atom shift in the cluster. In this shape, it is not the molecule as a whole that rotates, but the (CH₃)-group, because the iodine atom is bound under the intermolecular binding. Two single bands in gas-like state can be referred to the unbonded shape, in which the initial geometry of the molecule remains.

In the spectrum 2 (Fig. 2), recorded after the compression of inter-window distance to 1 mm, the band C with rotational structure and band A at 1260 cm⁻¹, which coincides in its position with the liquid phase band (Fig. 2, spectrum 3), remain. The rotational structure of the band C unambiguously indicates the formation of state with gaseous properties in the thin layer. After the extension of

the inter-window distance up to 6 mm, the spectrum has transformed instantly to the shape of spectrum 1 and returned to the spectrum 2 after the compression of the inter-window distance to 1 mm. Similar reversible transitions from a gas-like to a liquid-like state and back is typical for supercritical fluids when their density varies.

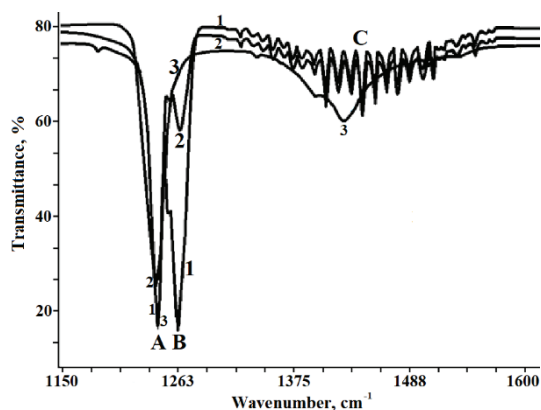


Fig. 2. Fragment of iodomethane spectra in H-C-H bending region. 1 – spectrum at 6 mm VTOC thickness; 2 – spectrum at 1 mm VTOC thickness; 3 – spectrum of liquid between KBr windows; A – band assigning to gas and liquid phases; B – band assigning to gas phase; C – band assigning to gas (with rotational structure) and liquid phases.

Tetrachloromethane

The gas-like state bands at 795 and 779 cm^{-1} (Fig. 3, bands A, D), assigning to the C-Cl bond stretching vibrations of tetrachloromethane, are observed in spectrum 1 (at the 6 mm optical distance). These bands have a different counter view: band A consists of several non-resolved components, and band D is a single band.

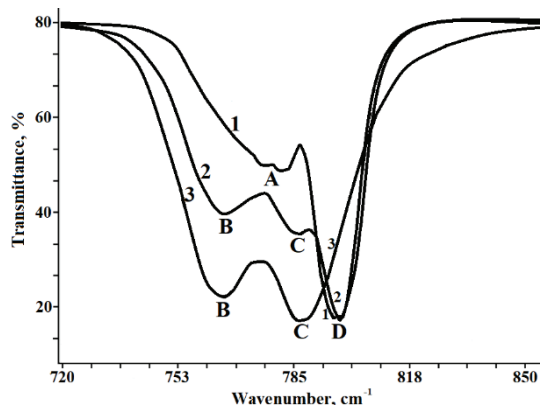


Fig. 3. Fragment of tetrachloromethane spectra in C-Cl stretching region. 1 – spectrum at 6 mm VTOC thickness; 2 – spectrum at 1 mm VTOC thickness; 3 – spectrum of liquid between KBr windows; A – band assigning to gas phase; B, C – bands assigning to liquid phase; D – band assigning to gas phase.

The arising of two C-Cl stretching bands instead of one band in accordance with selection rules (T_d symmetry point group) can be explained assuming the formation of different molecular structures in gas-like state as in the previous

case. The single band can be assigned to unbonded molecules, and the multi-component one – to the cluster shape, forming with chlorine atom shift under intermolecular binding, in which (CCl_3)-group rotates.

In spectrum 2 (Fig. 3) recorded at optical distance 1 mm, the gas-like state band D at 797 cm^{-1} and the liquid-like state bands C, B at 784 and 761 cm^{-1} , respectively, are observed. This spectrum changes negligibly after opening the cell ports. The spectrum recorded in a thin liquid layer between KBr windows (Fig. 3, spectrum 3) exhibits bands C and B at 788 and 765 cm^{-1} , respectively. The following optical distance extension up to 6 mm leads to the rapid reversible transition of the spectrum 2 into the gas-like spectrum 1 as it was observed for iodomethane. Since the boiling point of tetrachloromethane is relatively high, while the inter-window space available for evaporation is too small, the observed transformation of spectra cannot be caused by subsequent evaporation and condensation of the substance. Also taking into account that the small thickness of the cell excludes the IR manifestation of a regular gas spectra, this state can also be defined as fluid-like.

Dichloromethane

In the spectra of dichloromethane at the 6 mm optical distance, the gas-like state bands C, B (Fig. 4, spectrum 1) at 764 and 750 cm^{-1} , assigning to C–Cl bond stretching vibrations, are revealed. In the spectrum recorded at 1 mm VTOC thickness (Fig. 4, spectrum 2), the gas-like state band at 764 cm^{-1} , and the non-resolved liquid-like state band at 748 cm^{-1} were observed. The spectrum changes negligibly after opening the cell ports. The clearly manifested band A at 742 cm^{-1} is shown in spectrum 3 recorded in the thin layer of liquid between optical windows at ambient conditions.

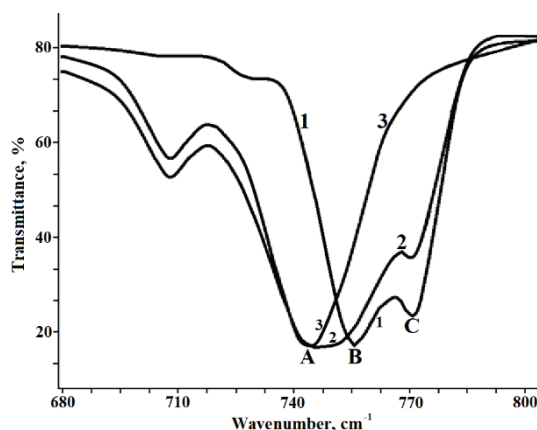


Fig. 4. Fragment of dichloromethane spectra in C-Cl stretching region. 1 – spectrum at 6 mm VTOC thickness; 2 – spectrum at 1 mm VTOC thickness; 3 – spectrum of liquid between KBr windows; A – band assigning to liquid phase; B, C – bands assigning to gas phase.

After the optical distance extension up to 6 mm, the gas-like state bands reappear, while the liquid-like state band is absent. Since, as already discussed,

the synchronous condensation-evaporation mechanism is less possible here, the presented IR data justify the fluid-like state formation.

Trichloromethane

The generation of the similar fluid-like state was spectrally confirmed under the VTOC compression-extension procedure for both trichloromethane (Fig. 5) and trichloromethane-d (Fig. 6). However, this pair of substances has some differences from other samples.

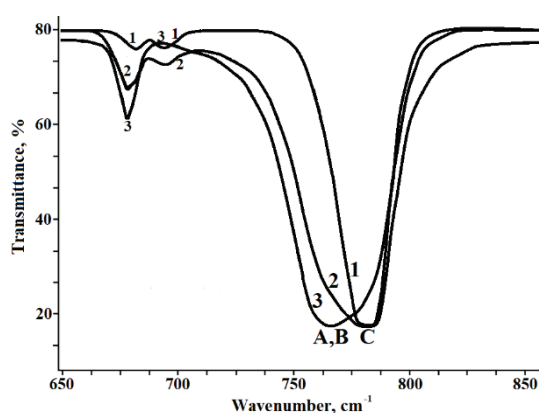


Fig. 5. Fragment of trichloromethane spectrum in C-Cl stretching region. 1 – spectrum at 6 mm VTOC thickness; 2 – spectrum at 1 mm VTOC thickness; 3 – spectrum of liquid between KBr windows; A, B – bands assigning to liquid phase; C – band assigning to gas phase.

A single gas-like state band C was detected in the spectrum recorded at 6 mm of VTOC thickness (Figs. 5 and 6, spectrum 1). The non-resolved liquid-like state bands A, B and the gas-like state band C assigning to C-Cl bond stretching vibrations were detected at 1 mm (Figs. 5 and 6, spectrum 2). The spectrum of liquid trichloromethane between KBr windows is presented as well (Fig. 5, spectrum 3).

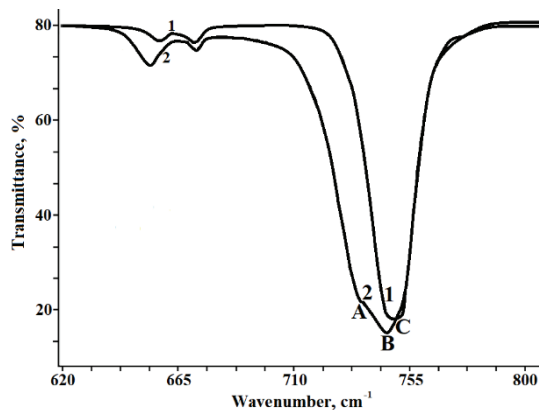


Fig. 6. Fragment of trichloromethane-d spectra in C-Cl stretching region. 1 – spectrum at 6 mm VTOC thickness; 2 – spectrum at 1 mm VTOC thickness; A – band assigning to liquid phase; B – band assigning to liquid phase; C – band assigning to gas phase.

The overlapping shape of the C–Cl stretching liquid bands' components can be caused by the formation of intermolecular hydrogen bond leading to the hydrogen atom shift,¹¹ unlike the molecular transformations with the participation of halogen atoms, causing stronger separation of C–Cl stretching bands in other systems.

CONCLUSION

The obtained data obviously indicate a phase state formation having a lot of similarities with the supercritical fluids; therefore, it can be defined as a “fluid-like state”. There are at least three main reasons for this conclusion. First, the spectrum of a true gas cannot be recorded at such a small thickness of the optical cell, as it was confirmed by many data of spectral practice. Second, there seems to be no dependence of the fluid-like state formation rate on the compound boiling point. Third, the gas–liquid state transition occurs rapidly and reversibly at compression–extension procedure, like in known fluid systems. Besides, this state remains inside the cell even without any tightness (when the plugs are removed), what would be impossible for regular gas.

It can be assumed that two different types of molecular structure – with unbonded molecules and a cluster shape, arising in the near-surface area (near optical window), are involved in the generation of the fluid-like state. Cluster shapes of molecules combine to form a dense layer, and unbonded molecules, being located around, maintain the required pressure, preventing the layer from disintegrating.

Thus, the obtained results confirm that the state with dual gas–liquid properties, or fluid-like state in other words, can be generated at ambient conditions not only for simple inorganic species, but also for organic systems.

ИЗВОД

ДЕТЕКЦИЈА ХАЛИДА МЕТАНА У СТАЊУ СЛИЧНОМ ТЕЧНОМ, ПРИ АМБИЈЕНТАЛНИМ УСЛОВИМА, ИНФРАЦРВЕНОМ СПЕКТРОСКОПИЈОМ

IOSIF GRINVALD и ROSTISLAV KAPUSTIN

*Nizhny Novgorod State Technical University n.a. R.E. Alekseev Minin str. 24,
603950 Nizhniy Novgorod, Russia*

У овом раду представљено је испитивање стања сличног течном, генерисаног при амбијенталним условима, за халиде метана (јодометан, тетрафлуорометан, трихлорометан и дихлорометан) ИС спектроскопијом. Показано је да при процедури компресије–ширења паре у спектралној ћелији променљиве дебљине, долази до формирања стања дуалне фазе које показује особине и гасова и течности. Утврђен је реверзибилни прелаз из облика сличног гасу у облик сличан течности, независно од термодинамичких карактеристика испитиваних халида метана.

(Примљено 26. априла, ревидирано 24. јуна, прихваћено 28. јуна 2021)

REFERENCES

1. E. S. Alekseev, A. Yu. Alentiev, A. S. Belova, V. I. Bogdan, T. V. Bogdan, A. V. Bystrova, E. R. Gafarova, E. N. Golubeva, E. A. Grebenik, O. I. Gromov, V. A. Davankov, S. G. Zlotin, M. G. Kiselev, A. E. Koklin, Y. N. Kononevich, A. E. Lazhko, V. V. Lunin, S. E. Lyubimov, O. N. Martyanov, I. I. Mishanin, A. M. Muzafarov, N. S. Nesterov, A. Yu. Nikolaev, R. D. Oparin, O. O. Parenago, O. P. Parenago, Y. A. Pokusaeva, I. A. Ronova, A. B. Solovieva, M. N. Temnikov, P. S. Timashev, O. V. Turova, E. V. Filatova, A. A. Philippov, A. M. Chibiryaev, A. S. Shalygin, *Russ. Chem. Rev.* **89** (2020) 1337 (<http://doi.org/10.1070/rcr4932>)
2. K. Tutek, A. Masek, A. Kosmalka, S. Cichosz, *Polymers* **13** (2021) 729 (<http://doi.org/10.3390/polym13050729>)
3. F. Maxim, K. Karalis, P. Boillat, D. T. Banuti, J. I. Marquez Damian, B. Niceno, C. Ludwig, *Adv. Sci.* **8** (2021) 2002312 (<http://doi.org/10.1002/adv.202002312>)
4. T. Wu, B. Han, in *Green Chemistry and Chemical Engineering. Encyclopedia of Sustainability Science and Technology Series*, B. Han, T. Wu, Eds., Springer, New York, 2019, p.173 (http://doi.org/10.1007/978-1-4939-9060-3_391)
5. G. N. Pack, M. C. Rotondaro, P. P. Shah, A. Mandal, S. Erramilli, L. D. Ziegler, *Phys. Chem. Chem. Phys.* **21** (2019) 21249 (<http://doi.org/10.1039/c9cp04101j>)
6. N. J. Hestand, S. E. Strong, L. Shi, J. L. Skinner, *J. Chem. Phys.* **150** (2019) 054505 (<http://doi.org/10.1063/1.5079232>)
7. B. K. Smith, *Infrared Spectral interpretation, a systematical approach*, CRC Press, Boca Raton, FL, 1999, p. 266 (<http://www.doi.org/10.1201/9780203750841>)
8. I. I. Grinvald, I. Yu. Kalagaev, A. N. Petukhov, R. V. Kapustin, *Rus. J. Phys. Chem.*, **A 93** (2019) 69 (<http://doi.org/10.1134/S0036024419130107>)
9. I. Grinvald, I. Kalagaev, A. Petukhov, A. Vorotyntsev, R. Kapustin, *Struct. Chem.* **30** (2019) 1659 (<http://doi.org/10.1007/s11224-019-01349-2>)
10. R. M. Stephenson, S. Malanowski, *Handbook of the Thermodynamics of Organic Compounds*, Springer, Dordrecht, 1987, p. 552 (<http://doi.org/10.1007/978-94-009-3173-2>)
11. I. I. Grinvald, I. Yu. Kalagaev, A. N. Petukhov, A. I. Grushevskaya, R. V. Kapustin, I. V. Vorotyntsev, *J. Struct. Chem.* **59** (2018) (<http://doi.org/10.1134/S0022476618020087>).