



Short communication

Raman scattering spectroscopic study of n-tetradecane under high pressure and ambient temperature

Xing Jian, Haifei Zheng*

Key Laboratory of Orogenic Belts and Crustal Evolution of Ministry of Education, School of Earth and Space Sciences, Peking University, Beijing 100871, PR China

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ABSTRACT

The Raman spectroscopy of n-tetradecane was investigated in a Moissanite anvil cell at pressure from 0.1 MPa to 1.4 GPa and ambient temperature. The result shows that the liquid–solid phase transition of n-tetradecane takes place at around 302.8 MPa and the corresponding ΔV_m obtained is about $-9.6 \text{ cm}^{-3}/\text{mol}$. Above 302.8 MPa, the frequencies of CH_2 and CH_3 symmetric stretching and asymmetric stretching vibration shift to higher wave numbers in a linear manner with increasing pressure, which can be expressed as: $\nu_s(\text{CH}_3) = 0.013P + 2882.0$; $\nu_{as}(\text{CH}_3) = 0.014P + 2961.6$; $\nu_s(\text{CH}_2) = 0.013P + 2850.8$; $\nu_{as}(\text{CH}_2) = 0.009P + 2923.2$. This relationship indicates that n-tetradecane can be a reliable pressure gauge for the experimental study within the pressure range of 0.3–1.4 GPa.

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1. Introduction

n-Tetradecane is one of the main components in petroleum [1–2]. The study on its chemical and physical properties, and the interaction between n-tetradecane and water at high pressure is of importance to the understanding of petroleum generation and hence petroleum exploration. However, the research on mixture of n-tetradecane and water under high pressure is limited. Yang et al. [3] studied solid–liquid phase equilibrium between 1-octanol and n-tetradecane under 220 MPa. Milhet et al. [4] investigated two binary systems – tetradecane + hexadecane and tetradecane + pentadecane under pressures up to 100 MPa using a polar microscopy device, but the pressures were not enough high. Takao Itoh [5] measured Fluorescence and excitation spectra of a polycrystalline solution of a,x-diphenyltetradecaheptaene in n-tetradecane at 77 K, but the room-temperature freezing pressure is still uncertain. Blas and Galindo [6] has studied phase behavior of CO_2 and n-tetradecane binary system under high pressure, but the diagram of phase transition and some thermodynamic parameters (such as ΔV_m) are still unclear.

Here, we present a new Raman spectroscopy study of n-tetradecane coexisting with water up to 1.4 GPa at ambient temperature by Moissanite anvil cell equipment.

2. Experimental method

The equipment used to generate high pressure is similar to Mao-Bell diamond anvil cell (DAC) [7], wherein a pair of Moissanite anvils replaced the usual diamond anvils. A hole of 0.35 mm in diameter in a stainless steel gasket of 1 mm thick was used as the sample chamber. Pure n-tetradecane (the volume percentage is about 10%, i.e., the volume of n-tetradecane is about $8.7 \times 10^{-3} \text{ mm}^3$) and water (the volume percentage is about 90%, i.e., the volume of water is about $7.8 \times 10^{-2} \text{ mm}^3$) were placed inside the sample chamber, and a small chip of quartz was used as the internal pressure gauge. The whole system was then sealed by compressing the two Moissanite anvils.

The Raman spectra were obtained by a Raman microspectrometer (Renishaw system RM-1000). The wavelength of excitation light was 514.5 nm (Argon ion laser operated at 20 mW). The objective was a Leitz 20 \times with a long working distance. The slit width was 50 μm and the corresponding spectra were 1 accumulation of 30 s each, and the range recorded was 50–4000 cm^{-1} .

During the experiment, we allowed a 2 min interval [4,15,16] after compressing the sample before measuring the Raman spectra in order to keep the sample in a pressure equilibrium state. The Raman spectra of the quartz (the pressure gauge), water and n-tetradecane were measured by the Raman microspectrometer, respectively. In this experiment, in order to obtain the system pressure after each compression, we took the exciting laser spot on the quartz first, then moved it on water and n-tetradecane successively. For each compression, a photo

* Corresponding author. Tel.: +86 10 62758223.

E-mail address: hfzheng@pku.edu.cn (H. Zheng).

Table 1
The data of Raman spectra at high pressure.

Number	Pressure (MPa)	ν_{2858}	ν_{2894}	ν_{2928}	ν_{2958}	ν_{H_2O}
1	108.5	2858.6	2894.4	2928.7	2958	3422.1
2	111.5	2858.4	2893.7	2926.7	2956.2	3423.4
3	165.8	2858.3	2893.9	2927.8	2958.1	3431.4
4	235.7	2858.5	2893.7	2928.2	2961.1	3423.1
5	270.8	2858.3	2893.2	2928.1	2959.9	3419.7
6	302.8	2854.1	2885.9	2926.3	2966.3	3422.3
7	403.9	2855.1	2886.7	2925.5	2965.6	3418.7
8	442.4	2856.4	2887.6	2927.9	2968.8	3414.8
9	522.7	2857.5	2888.4	2928.6	2970	3410.4
10	545	2857.6	2889.2	2928.4	2967.7	3419.7
11	626.7	2858.3	2890.5	2929.5	2971.2	3419.6
12	637.8	2859.6	2891.1	2929.7	2970.9	3408.2
13	696.7	2859.7	2891.7	2929.5	2971.2	3418.8
14	717.8	2861.2	2892.6	2930.6	2973.5	3417.1
15	734.8	2860	2889.8	2928.8	2969.2	3410.2
16	775.1	2860.4	2892.2	2930.5	2972.7	3411.4
17	779.5	2860.7	2892.1	2929.8	2970.6	3411.9
18	782.4	2861.2	2893.4	2931.2	2974.4	3423.2
19	799.6	2861.5	2893.2	2931.2	2974.4	3419.3
20	867.7	2861.8	2892.6	2931.3	2974.5	3409.4
21	865.2	2861.9	2891.7	2930.5	2971.9	3414.7
22	859.6	2861.8	2891.9	2930.5	2973	3410.1
23	904.8	2862.6	2892.3	2931.5	2973.6	3413.5
24	912.9	2862.5	2894.2	2932.5	2976.5	3415.7
25	932.4	2863.4	2894.8	2931.2	2974.8	3421.6
26	942.7	2862.8	2893	2933	2977.6	3414.2
27	995.7	2863.7	2895.4	2932.5	2977.4	3405.7
28	1017	2864.3	2896.9	2933.2	2977.6	3419.3
29	1129	2865.5	2896.8	2934.1	2979.4	3413.5
30	1123	2865.6	2897.5	2935.7	2980.2	3401.8
31	1229	2866.7	2898.4	2935.3	2981	3414.9
32	1219	2865.8	2896.4	2934.1	2977.5	3400.3
33	1217	2865.6	2897.9	2934.1	2975.4	3210.6
34	1369	2867.4	2899.5	2935.4	2979.5	3198.7

was taken so as to determine the phase transition of the sample.

According to the studies of Schmidt and Ziemann [8], the experimental pressure was calculated by

$$P(\text{MPa}) = 0.36079[(\Delta\nu_p)_{464}]^2 + 110.86(\Delta\nu_p)_{464} \quad (1)$$

where $(\Delta\nu_p)_{464}$ is the wave number shift relative to the line position of 464 cm^{-1} at 0.1 MPa ($0 < (\Delta\nu_p)_{464} \leq 20 \text{ cm}^{-1}$). The pressure calculated by Eq. (1) has an uncertainty of $\pm 50 \text{ MPa}$.

3. Results and discussion

By fitting the spectra data with Peakfit software, the results of Raman shift and pressure are obtained and listed in Table 1. Fig. 1 shows parts of the spectra at different pressures. It can be seen that at the pressure above 270.8 MPa the spectra has an abrupt change, indicating the phase transition of the n-tetradecane from liquid to solid. It is consistent with the observation from microscope that the crystals of n-tetradecane appeared at the pressure above 270.8 MPa , which is shown in Figs. 2 and 3 (in Fig. 2, the spheres similar to bubbles are n-tetradecane glomeration in the n-tetradecane region actually).

n-Tetradecane possesses a great number of Raman bands [9], reflecting the complexity of its internal vibrations. In general, the stronger Raman bands are the CH_3 symmetric and asymmetric stretching vibrations, $\nu_s(\text{CH}_3)$ and $\nu_{as}(\text{CH}_3)$, CH_2 symmetric and asymmetric stretching vibrations, $\nu_s(\text{CH}_2)$ and $\nu_{as}(\text{CH}_2)$, the CH_3 asymmetric bending vibrations, the $-(\text{CH}_2)_n-$ in-phase twisting vibrations and C–C framework vibrations [10–13]. However, some of these Raman bands are too weak, so we only discuss the CH_3 and CH_2 stretching vibrations. According to previous reports, the Raman shifts of $\nu_s(\text{CH}_3)$, $\nu_{as}(\text{CH}_3)$, $\nu_s(\text{CH}_2)$, $\nu_{as}(\text{CH}_2)$ are 2894 cm^{-1} ,

2958 cm^{-1} , 2858 cm^{-1} , 2928 cm^{-1} , respectively at 1 atm and ambient temperature.

Before the phase transition, i.e. when the system pressure below 302.8 MPa , the relations between pressure and frequency of the stretching vibrations are given as:

$$\nu_s(\text{CH}_3) = -0.0046P + 2894.6 \quad (2)$$

$$\nu_{as}(\text{CH}_3) = 0.0221P + 2954.7 \quad (3)$$

$$\nu_s(\text{CH}_2) = -0.0008P + 2858.6 \quad (4)$$

$$\nu_{as}(\text{CH}_2) = 0.0029P + 2927.4 \quad (5)$$

For the data at the pressure lower than 302.8 MPa , the frequency of CH_2 and CH_3 asymmetric stretching vibration also shift to higher wave numbers with increasing pressure, but the symmetric stretching vibration shift to lower wave numbers. Because there are only five data points at the pressure less than 302.8 MPa , the relations between Raman shift and pressure are not obtained.

At the pressure above 302.8 MPa , Fig. 1 also shows that the peak intensity of symmetric and asymmetric stretching vibration of CH_3 increases significantly after phase transition, compared with CH_2 . It shows that the polarity and electronegativity of CH_3 bond increase suddenly, so does Raman-active of CH_3 bond. But these properties of CH_2 have no remarkable change before and after phase transition. All Raman bands shift to higher wave numbers linearly with increasing pressure (Figs. 4 and 5). The relations between pressure and frequency of the stretching vibrations are given as following:

$$\nu_s(\text{CH}_3) = 0.013P + 2882.0 (r = 0.966) \quad (6)$$

$$\nu_{as}(\text{CH}_3) = 0.014P + 2961.6 (r = 0.914) \quad (7)$$

$$\nu_s(\text{CH}_2) = 0.013P + 2850.8 (r = 0.99) \quad (8)$$

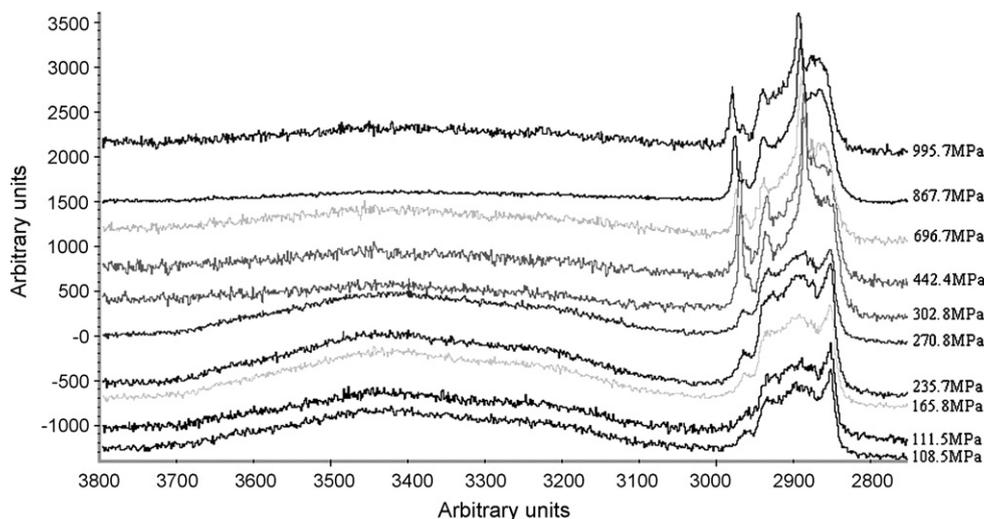


Fig. 1. Raman spectra of CH₃, CH₂, O–H stretching vibrations at different pressure.

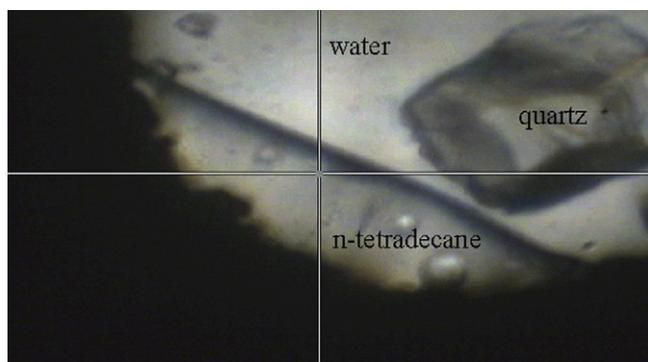


Fig. 2. The state of the sample before phase transition.

$$\nu_{as}(\text{CH}_2) = 0.009P + 2923.2 (r = 0.959) \quad (9)$$

According to Eqs. (6) and (8), they have the same slope (0.013), indicating that CH₃ and CH₂ symmetric stretching vibrations have the same sensitivity to pressure variation; whereas the slope of Eq. (7) is larger than that of Eq. (9), showing that CH₂ asymmetric stretching vibration have lower sensitivity to pressure change compared with CH₃.

The correlation coefficient ($r=0.99$) of Eq. (8) shows that the linear relation has a smaller scatter than others, which are also shown in Figs. 4 and 5. Therefore, n-tetradecane is reliable as a pressure gauge for high-pressure experimental study. The formula

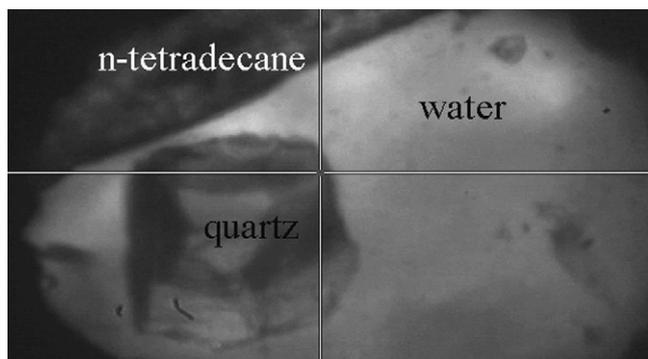


Fig. 3. The state of the sample after phase transition.

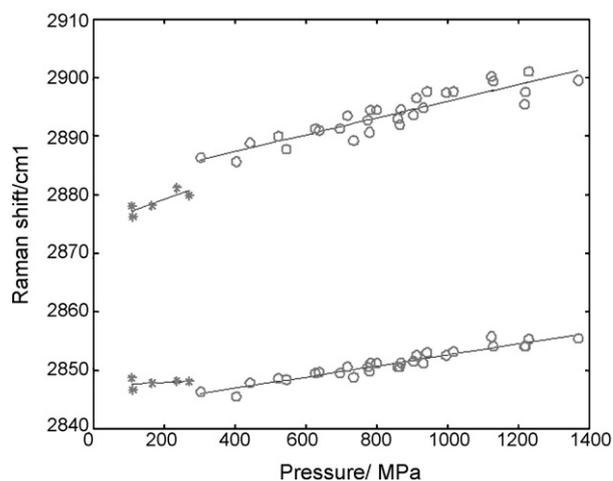


Fig. 4. The relation between the wave number of CH₃ and CH₂ asymmetric stretching vibration peaks and system pressure.

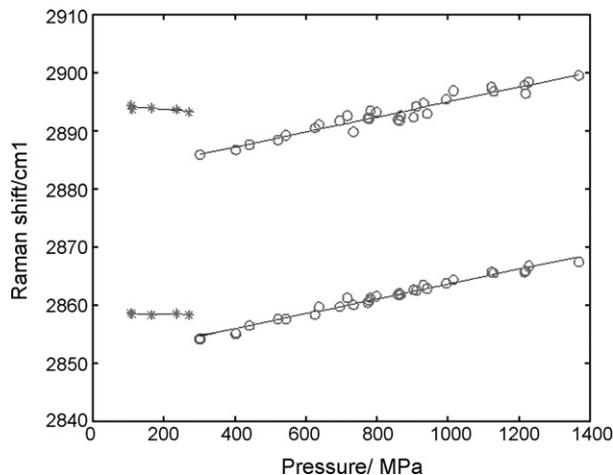


Fig. 5. The relation between the wave number of CH₃ and CH₂ symmetric stretching vibration peaks and system pressure.

Table 2
Liquid–solid equilibrium point measured in previous and present study.

	n-Tetradecane	n-Pentane	n-Hexane	1-Dodecene
Equilibrium point <i>P</i> (MPa) at 0.1 MPa				
<i>P</i> (MPa)	0.1	0.1	0.1	0.1
<i>T</i> (K)	279	144	178	238
Equilibrium point at ambient temperature				
<i>P</i> (MPa)	300	1900	1400	500
<i>T</i> (K)	298	300	296	294

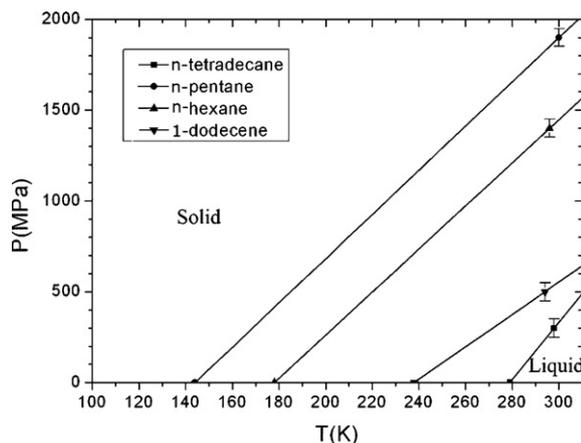


Fig. 6. Liquid–solid phase diagram of n-tetradecane, n-pentane, n-hexane and 1-dodecene.

of the pressure gauge is as following (from 0.3 GPa to 1.4 GPa):

$$P = 76.9v_s(\text{CH}_2) - 2.19 \times 10^5 \quad (10)$$

The uncertainty is only ± 32 MPa.

Based on the freezing point ($+5.8^\circ\text{C}$ [14]) of n-tetradecane at 1 atm and the freezing pressure (302.8 MPa) at 25°C . In comparison with the previous studies on n-pentane [15], n-hexane [16] and 1-dodecene [17], the results are shown in Table 2. Based on the date, the phase diagram of n-tetradecane can be obtained (Fig. 6). Compared our study with previous studies, Fig. 6 illustrates the similarity of the liquid–solid phase transition curves among alkanes, and the difference between alkanes and olefins (base on the slope of these curves). Further studies are required to make clear the relations. According to the Clapeyron equation:

$$dp/dT = \Delta H_m / T \Delta V_m \quad (11)$$

where dp/dT (15.76 MPa/K obtained in this study) is the slope of the phase transition curve, ΔH_m and ΔV_m are the molar enthalpy and molar volume changes respectively in the phase transition. Known that ΔH_m equals -45.07 kJ/mol [14],

$\Delta V_m = -9.6$ cm³/mol is estimated. Considering the error of pressure, ΔV_m is $-11.5 \sim -8.2$ cm³/mol.

4. Conclusion

From the experimental study, we came to the following conclusions:

- (1) The CH₃ and CH₂ symmetric stretching vibration and asymmetric stretching vibration of solid phase shift to higher wave numbers linearly with increasing pressure.
- (2) n-Tetradecane is a reliable pressure gauge for high-pressure experimental study from 0.3 GPa to 1.4 GPa.
- (3) The liquid–solid phase transition of n-tetradecane occurred at around 302.8 MPa. Its molar volume change, ΔV_m equals about -9.6 cm³/mol.

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