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Raman Spectroscopic Studies of Pressure-Induced Phase Transitions on 1-Dodecene *

DU Zhi-Xue(杜治学), ZHENG Hai-Fei(郑海飞)**

Key Laboratory of Orogenic Belts and Crust al Evolution of Ministry of Education, School of Earth and Space Sciences, Peking University, Beijing 100871

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Raman spectroscopic features of 1-dodecene are studied in a moissanite anvil cell up to 3.0 GPa at 21°C. Our data indicate that 1-dodecene is chemically stable under the experimental condition because no new Raman peaks can be observed. However, two significant discontinuities in the plots of Raman shift versus pressure indicate two phase transitions of 1-dodecene. One is liquid–solid transition at pressure of about 500 MPa, the other is solid–solid phase transition at pressure from 1300 to 1550 MPa. The latter is considered to be related to the orientational change of the plane structure of ethylene. A rudimentary phase diagrams for 1-dodecene, n-pentane, n-hexane are proposed based on the results and previous data.

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Recently, pressure induced phase transitions of alkanes have been examined. At ambient temperature, liquid–solid phase transitions for n-hexane, n-pentane and n-heptane were observed at 1.4 GPa,[1] 1.9 GPa,[2] 1.5 GPa,[3] respectively. Especially, for n-pentane, solid–solid phase transition was determined at 7.5 GPa, which is proposed to be an orientational order-disorder transition driven by the dampening of the rotation of the methyl group.[3] Liquid–solid phase transition of dibromoethylene is located at 1.7 GPa, and two solid–solid phase transitions are observed at 7.1 GPa and 12.5 GPa, respectively, which are attributed to the chemical transformation of dibromoethylene.[4] So far, behaviour of the C=C bond at high pressure is poorly understood.

Raman spectroscopy is a valuable tool for understanding intermolecular interactions and phase transition of molecular solids.[5−8] High pressure Raman scattering is useful to study lattice dynamics and mechanism of pressure-induced crystalline-to-crystalline and crystalline-to-amorphous transformations. Here we present a high pressure experiments with *in situ* Raman spectroscopy measurement to discuss the properties of 1-dodecene, especially the behaviour of the C=C bond at high pressure.

The structure of high press apparatus is similar to that of the Mao-Bell diamond anvil cell (DAC,[9] but the diamond anvils are replaced by moissanite anvils. A small quartz chip was loaded into a hole bored in the stainless steel gasket (1.0 mm in thickness and 0.25 mm in diameter) as an internal pressure gauge, and commercial 1-dodecene (from Alfa Aesar, 95%, without further purification) was also enclosed. Pressure in the sample chamber was gradually increased between two moissanite anvils. Raman spectra were recorded simultaneously with a Renishaw 1000 spectrometer. An argon-ion laser provided the excitation light source, with an output of 50 mW at 514.5 nm. All high-pressure spectra were taken at room temperature. The transparency of moissanite allows *in situ* observation for the sample under an optical microscope. Photographs of the sample chamber can also be taken.

Pressure in the chamber is calculated according to the following formula given by Schmidt *et al.*:[10]

$$P(\mathrm{MPa}) = 0.36079(v_p - 464)^2 + 110.86(v_p - 464),$$

where v_p is the Raman wave number of quartz under the applied pressure and 464 is the Raman wave number of quartz in ambient environment.

Table 1. Data of Raman shift and the calculated result of 1-dodecene. Here $d\omega/dP$ (cm^{-1}/GPa) denotes the pressure derivative of Raman frequencies for the various modes of 1-dodecene in three different phases, extracted from Figs. 2 and 3 by linear fitting.

Vibrational modes	Raman Shift (cm^{-1})	$d\omega/dP(\mathrm{cm}^{-1}/\mathrm{GPa})$			
		Liquid	Solid I		Solid Ⅱ
		Fig. 2	Fig. 2	Fig. 3	Fig. 3
V(-$(CH_2)_n$-)	1300	2.3 ± 0.3	$3.0 + 0.1$	$3.1 + 0.1$	Same as solid I
V_s(C=C)	1642	4 ± 2	6.0 ± 0.4	5.3 ± 0.4	1.5 ± 0.2
$V_s(CH_2)$	1655	4.1 ± 0.3	13.4 ± 0.2	14.0 ± 0.1	Same as solid I
$V_s(=CH_2)$	3000	11.3 ± 0.3	11.9 ± 0.5	11.6 ± 0.4	6.0 ± 0.3
$V_{as}(=CH_2)$	3080	13.1 ± 0.5	15.8 ± 0.6	14.3 ± 0.8	8.5 ± 0.5

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**To whom correspondence should be addressed. Email: hfzheng@pku.edu.cn

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Raman scattering experiments for 1-dodecene were conducted at 21°C and pressure up to 3.0 GPa.

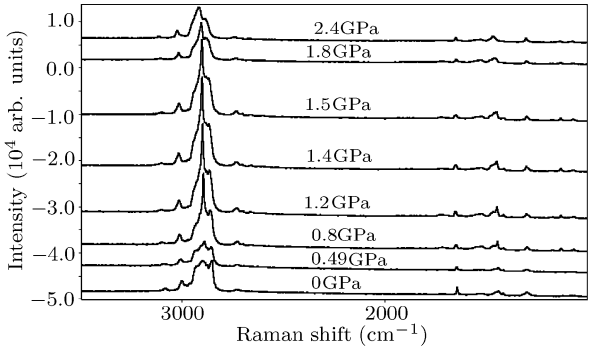


Fig. 1. Raman spectra of 1-dodecene at pressures up to 2.4 GPa.

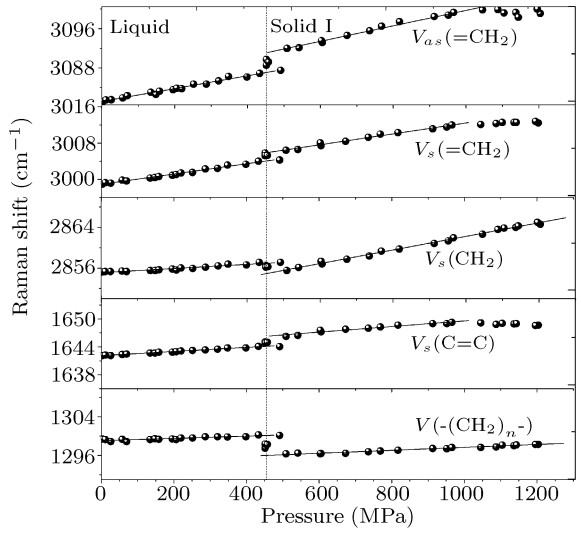


Fig. 2. Raman shifts discontinuities of some vibrational modes of 1-dodecene at the pressures up to 1.2 GPa, showing the liquid–solid phase transition at about 500 MPa.

The Raman spectrum of 1-dodecene is similar to that of 1-butene. According to Ref. [11], the assignment of several Raman peaks of 1-dodecene is listed in Table 1. In the range of the experimental pressures, there are two sections for the Raman spectra in the range of 1000–3500 cm^{-1} (Fig. 1).

For the liquid–solid phase transition, Fig. 2 shows a discontinuity in Raman shifts as a function of pressure at about 500 MPa, of which the characteristic is consistent with previous Raman studies of liquid–solid phase transitions.[1,2] Firstly, a sharp break exists in the plot of Raman frequency versus pressure. Secondly, optical microscopic observations show that the sample turned dark from total transparency.[12] Thirdly, the width of the Raman peak drops significantly. Therefore, it is concluded that 1-dodecene experiences a liquid–solid phase transition around 500 MPa at room temperature. The solidification pressure of 1-dodecene is much lower than hexane[1] and n-pentane,[2] which is attributed to the larger molecular weight of 1-dodecene.

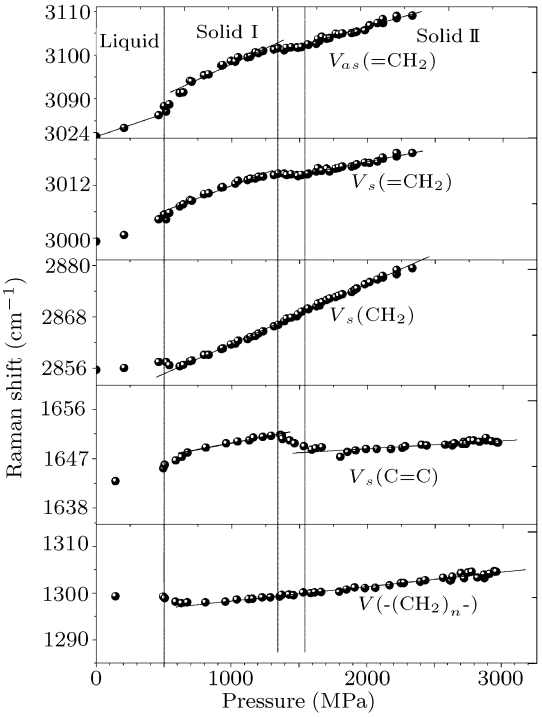


Fig. 3. Raman shifts of some vibrational modes of 1-dodecene at the pressure up to 3.0 GPa, showing a solid–solid phase transition at 1300–1500 MPa.

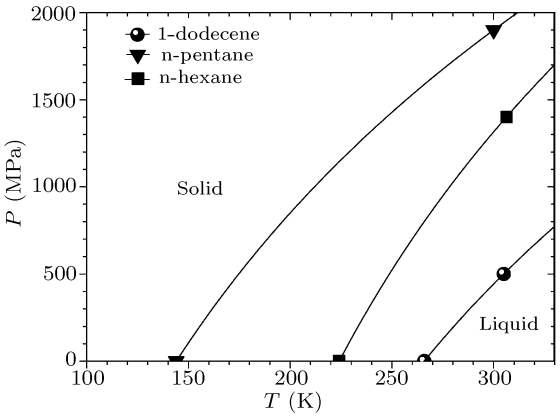


Fig. 4. Phase diagram of 1-dodecene, n-pentane and n-hexane.

For the solid–solid phase transition, the Raman bands of different vibration models, $V_{as}(=CH_2)$, $V_s(=CH_2)$ and $V_s(CH_2)$, between 2500 and 3000 MPa, are discarded because their frequencies are the same as those of the C-H region and the signals are too weak for data analysis. This can also be justified by the fact that the relative errors of $V(C=C)$ and $V(-(CH_2)_n-)$ become larger at the pressure above 2500 MPa.

The frequencies of $V_{as}(=CH_2)$, $V_s(=CH_2)$, and $V(C=C)$ in Fig. 3 show obvious sudden changes at

about 1300 MPa and 1550 MPa. However, no similar change occurs at the frequencies of $V_s(CH_2)$ and $V(-(CH_2)_n-)$. Consequently, the abrupt changes of frequencies are only related to the C=C bond. It can be inferred that the Raman spectroscopic changes result from the orientation change of plane structure of ethylene.

The points between the lines for liquid and solid I in Fig. 2 indicate the mixture of liquid and solid I, i.e. the liquid is not completely transformed to solid I.

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

		1-dodecene (this work)	n-pentane[1]	n-hexane[2]
Equilibrium Point at 0.1 MPa[13]	P(MPa)	0.1	0.1	0.1
	T(K)	238	144	178
Equilibrium Point at ambient temperature	P(MPa)	500	1900	1400
	T(K)	294	300	296
$\Delta H_m/\Delta V_m$ (GPa)		2.4	2.6	2.8

On the other hand, the region from 1300 MPa to 1550 MPa consists of 5 experimental data at the transition. We assume that the region from 1300 MPa to 1550 MPa represents a mixture of solid I and solid Ⅱ. That is, accomplishment of the solid–solid phase transition takes a longer time than that of the liquid–solid phase transition that consists of only two or three transition points (Fig. 2).

Based on the data in Table 2, the phase diagram for 1-dodecene, n-pentane and n-hexane can be calculated by the Clausius–Clapeyron relation. The constructed phase diagram is shown in Fig. 4.

In summary, at the temperature of 21°C, 1-dodecene undergoes a liquid–solid phase transition around 500 MPa. A solid–solid phase transition occurs between 1300 MPa and 1550 MPa due to changes of structure of the C=C bond, which is probably related to orientational changes of plane structure of ethylene.

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