

Raman Spectral Characteristic Analysis of Natural Gas Hydrate Decomposition Process

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Abstract: Natural gas hydrate is an important potential energy source. Hydrates are easy to decompose at room temperature and pressure. In this paper, the laser Raman technology is used to quickly detect mixed gas hydrates at room temperature. The spectral characteristics show that: (1) The peak area ratio of the Raman spectrum is analyzed to obtain the mixed gas hydrate. The structure is type II, the stretching vibration or rotation region of the *C-C* bond is 700~2500cm⁻¹, the stretching vibration region of the *C-H* bond is 2850~3000cm⁻¹, and the stretching vibration region of the *O-H* bond is 3000~3800cm⁻¹; (2) Observing the change of *C-H* bond energy with time shows that the bond energy of hydrates prepared in the laboratory gradually decreases with the passage of time under normal temperature and pressure, and the peak disappears; (3) Spectral peaks and Raman patterns identified by combining with wavelet analysis theory build a natural gas hydrate analysis library. In the process of natural gas hydrate extraction and transportation, the application of laser Raman technology does not require any sample processing, and the detection process can be fast, convenient and accurate. This technology provides an effective detection, analysis and evaluation method for hydrate state research. Combined with wavelet analysis, Raman spectroscopy can be used for online detection in the process of hydrate mining and transportation, providing a convenient detection method for hydrate research.

Keywords: Natural Gas Hydrate, Raman Spectrum, Characteristic Peak, *C-H* Bond, Wavelet Transform

1. Introduction

Natural gas hydrate mainly exists in the marine continental margin and the permafrost area of the land. It is an unconventional natural gas resource with the characteristics of wide distribution, large reserves and high energy. Therefore, it has been studied by many experts and scholars. It can be used as a new energy for people to use [1]. Natural gas hydrate is mainly composed of methane and water molecules in a low temperature and high pressure environment to form solid substances, where in the hydration number (*n*) is the number of moles of water molecules that form a hydrate with 1 mol of methane molecules [2], and CH₄·*n*H₂O formed by methane gas is the most widely distributed, and its reserves account for about 90% of hydrate reserves. Natural gas hydrate can transport and store a large amount of gas, and the accurate determination of hydrate is of great significance to the exploitation, research and industrial application of unconventional resources.

Although natural gas hydrate is known as a new type of energy, its theoretical research is still in the basic stage, and the future mining development of hydrate needs to be supported by a large number of experimental studies. At present, the research direction of hydrate in China mainly focuses on the formation and decomposition process of hydrate. By controlling the pressure and temperature of hydrate formation, the decomposition and formation process of hydrate can be observed from a macro perspective [3-5]. With the diversity of analytical instruments, advanced experimental devices such as Raman, nuclear magnetic resonance and polarized light microscopes have been widely used in hydrate research. Hydrate research is more precise.

With the advancement of modern analysis methods, laser Raman technology has been widely used in the study of hydrate dynamics with advanced observation and testing methods, and has gradually become an effective method for the microscopic detection of hydrates. In 1975, laser Raman spectroscopy was used for the first time in the research process

of halogen hydrate. Using Raman spectrometer to illuminate the hydrate can analyze the structure, composition, cage occupancy and hydration number of the hydrate through the spectrum and the peaks of each bond. Compared with other detection instruments, laser Raman meters have a wider application range [6-8]. However, our theoretical research on natural gas hydrate is still very weak, and it is urgent to develop relevant experimental analysis techniques to serve the theoretical research of gas hydrate. Domestic experiments on the formation and decomposition of hydrates are mostly carried out in macroscopic reactors. The formation and decomposition process of hydrates in the system are determined by changes in temperature and pressure, and the microscopic details of hydrate formation and decomposition cannot be observed. Dynamics research is developing in a more refined and precise direction.

In this paper, the method of laser Raman spectroscopy is used to analyze the hydrates synthesized in the laboratory on a macroscopic level. It is the focus of this research that the hydrates can be quickly identified by detecting the peaks of chemical bonds. This experiment and research results provide a convenient online detection method for monitoring the hydrate state during hydrate extraction and transportation in the future. The Raman spectrum database of hydrate is established by combining Raman spectroscopy and wavelet analysis, to do preliminary basic work for the rapid detection of hydrates in deep water and transportation pipelines in the future.

2. Experimental Part

2.1. Instruments and Reagents

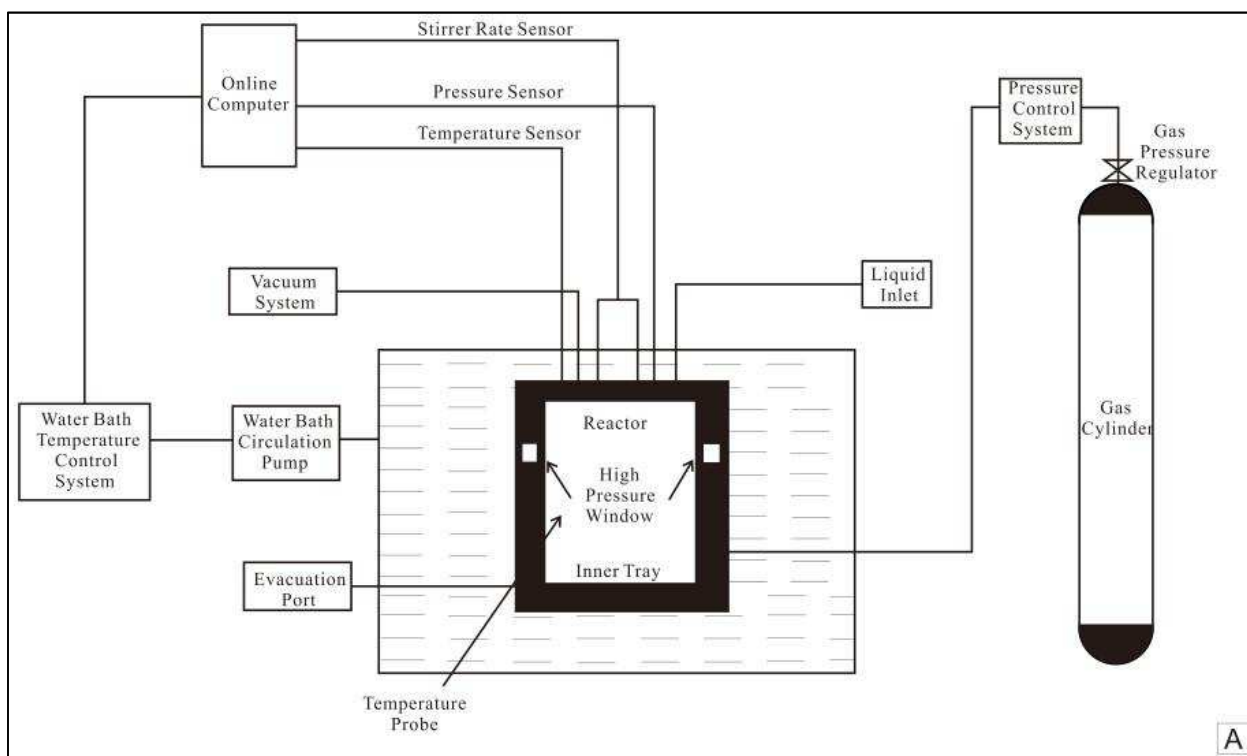
In the preparation of natural gas hydrate, the experimental

drugs used sodium dodecyl sulfate (SDS) with a purity of $\geq 86\%$; mixed gas containing 85.9% methane; laboratory-made deionized water. The experimental instrument for hydrate generation needs to simulate the low temperature and high pressure environment in deep sea or permafrost area, so *KDSC-II* type natural gas hydrate multi-functional simulation device is used, which consists of four systems. Natural gas hydrate is generated in the reactor, the schematic diagram of the multi-functional simulation equipment for *KDSC-II* gas hydrate is shown in Figure 1, A. The laser Raman equipment uses the *SSR-200* portable Raman instrument for experiments (Figure 1, B). The specific parameters are shown in Table 1.

Table 1. Basic parameters of *SSR-200* laser Raman spectrometer.

SSR-200	Parameters
Spectral range	150-4300
Spectral resolution	$\leq 10\text{cm}^{-1}@1777\text{cm}^{-1}$
signal to noise ratio	$\geq 400: 1@100\text{ms}$
Excitation wavelength	$785\pm 0.5\text{nm}$
Detection time	10ms-2min
Fiber Probe	Detachable objective lens
Weight	$< 3\text{kg}$
Size	$235\text{mm}\times 110\text{mm}\times 190\text{mm}$

Figure 1, the autoclave in C is mainly a hydrate generation device. The effective volume is 350ml. The reaction kettle is made of high-pressure and low-temperature resistant stainless steel. The pressure in the container should be less than 25MPa, and the temperature should not be higher than 90°C and not lower than -10°C . The temperature is controlled by a constant temperature water bath with an accuracy of $\pm 0.1\text{K}$; the pressure is controlled by a pressure detection device for the gas injected into the reactor, with an accuracy of $\pm 0.01\text{MPa}$.



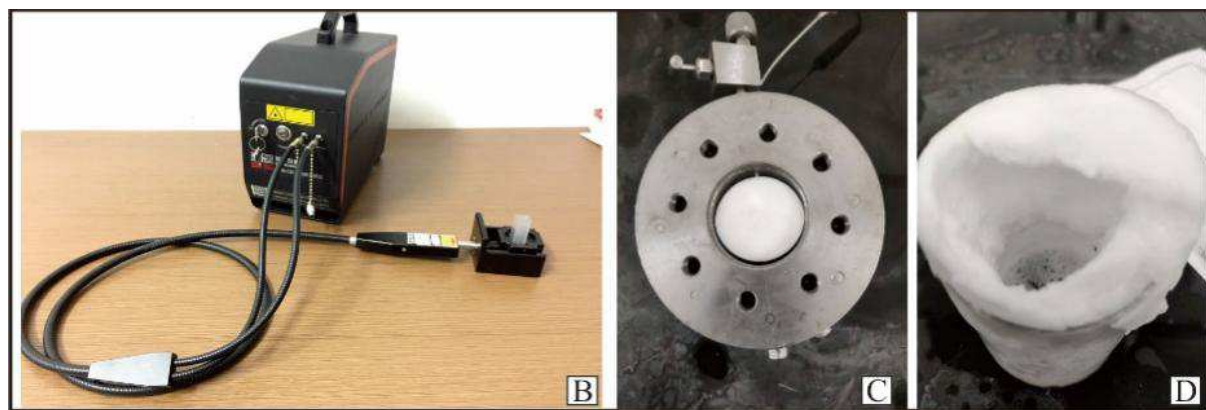


Figure 1. Hydrate test equipment and experimental preparation results.

A: KDSC-II type natural gas hydrate multifunctional simulation experimental device; B: SSR-200 portable Raman spectrometer; C: Natural gas hydrate generated in the reactor; D: The hydrate in a plastic container at room temperature.

2.2. Experimental Steps

- (1) Deionized water is prepared in the laboratory, and 0.03g of sodium dodecyl sulfate is fully mixed with 100ml of deionized water to prepare SDS solution;
- (2) In order to facilitate the removal and detection of hydrates, a 5.5cm×6.5cm plastic container was made to ensure that it could be placed in the reactor to clean the experimental equipment multiple times, and dried with a dryer to avoid the original residual magazine and the interference of other water sources makes the prepared hydrate impure;
- (3) Pour the prepared SDS solution into a plastic container, and put the plastic container into the reaction kettle. Seal the reaction kettle and check the air tightness to ensure that there is no air leakage in the reaction kettle, and use a vacuum device to evacuate the reaction kettle to a vacuum state;
- (4) Fix the reaction kettle on the operating platform of the KDSC-II experimental equipment, and use the lifting device to slowly put the reaction kettle into a 2°C water bath, so that the water surface completely covers the reaction kettle. The methane gas with a purity of 85.9% is injected into the reactor by the air inlet system, and the injection of the mixed gas is stopped when the pressure sensor shows 7MPa;
- (5) Open the data acquisition software on the online computer, continuously record the temperature and pressure changes in the reactor, wait for 8 hours, observe the pressure gauge after 8 hours, wait for the pressure gauge to remain stable for 2 hours, and observe the high pressure window of the reactor you can see solid formation. The preparation is over;
- (6) Take out the reaction kettle from the water bath, and depressurize it. When the internal pressure of the reaction kettle drops to 1 MPa, open the reaction kettle and take out the plastic container containing the hydrate;
- (7) Bring the plastic container containing the hydrate to

room temperature (Figure 1, D), and use the laser Raman instrument to irradiate different positions of the hydrate to obtain the peak at this time, record the time, and repeat this step until the hydrate disappeared at room temperature.

3. Analysis and Discussion of Experimental Results

In order to quickly and conveniently measure the Raman spectral characteristics of hydrates, this experiment was carried out at room temperature. Since hydrates mainly exist in an environment of low temperature and high pressure, hydrates will decompose rapidly in the environment of room temperature and normal pressure. Therefore, Raman spectroscopy equipment is used to quickly analyze the samples until the peaks unique to C-H bonds in natural gas hydrates cannot be detected.

3.1. Structural Characteristics of Hydrates

Through the research on the classification of hydrate types, hydrates are currently divided into three categories according to the number of water molecules and gas molecules they are composed of. The ratio of water molecules to gas molecules in type I hydrates is 23:4, showing a cubic structure; the ratio of water molecules to gas molecules in type II hydrates is 17:3, showing a rhombus structure; the ratio of water molecules to gas molecules in type H hydrates is 17:3, showing a hexagonal structure [9-14]. The Raman shifts of C-H bond and O-H bond stretching vibration in hydrates were detected by laser Raman to classify hydrate types [15-18]. Since the intensity of Raman spectra is proportional to the number of molecules in the hydrate [19-23], the ratios of large cages to small cages in class I and class II hydrates are 3:1 and 1:2 respectively. The structure type of the hydrate can be well identified by analyzing the Raman spectrum.

According to the hydrate prepared in the laboratory, the measurement was carried out at room temperature, and the Raman spectra of four time points were selected, and the

time interval was 5 min, as shown in Figure 2. There are mainly three types of peaks of natural gas hydrates. The Raman shift of the stretching vibration of the *O-H* bond obtained by the combination of gas molecules and water molecules in the hydrate is around 3218 cm^{-1} . In natural gas hydrate, a CH_4 molecule can only enter into a cage formed by

a water molecule relying on hydrogen bonds. According to the Raman spectrum measured by the experiment, it can be seen that the large cage and the small cage have peaks at 2901 cm^{-1} and 2913 cm^{-1} , and the peak area ratio is 1:2. It can be judged that the hydrate prepared in this laboratory is II type structure.

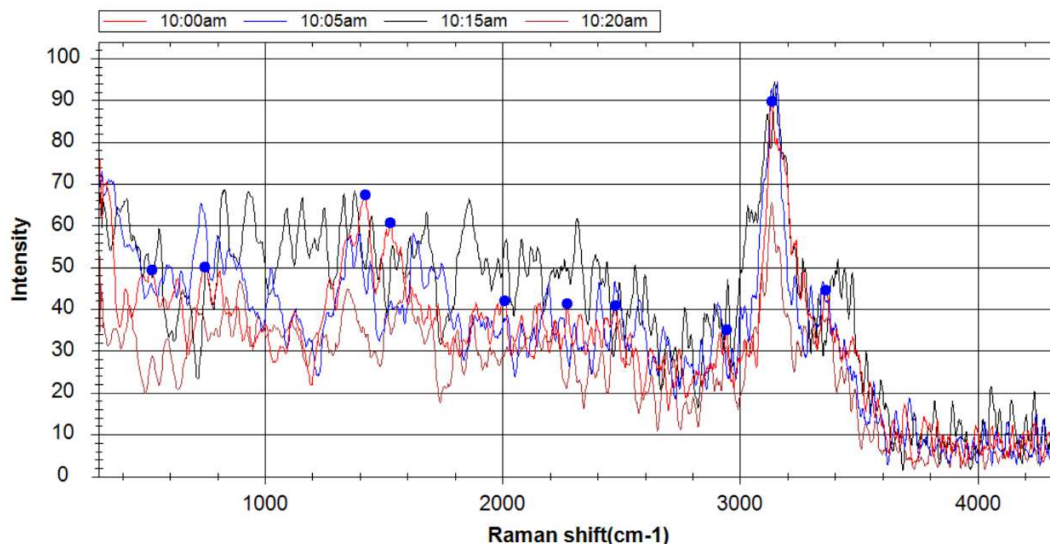


Figure 2. Comparison of Raman peaks at different times.

3.2. Raman Spectral Characteristics of Hydrate Samples

In order to accurately analyze the Raman spectral characteristics, different test points were selected for the hydrate test. The Raman spectrum of the test hydrate is shown in Figure 3. From the Raman spectrum, it can be seen that the spectral peaks in the hydrate roughly divide the spectrum into three regions [24-25]: the stretching vibration of the *C-C* bond in the hydrate is mainly in the range of $700\sim 2500\text{ cm}^{-1}$; The

C-H bond stretching vibration range that plays a decisive role in hydrate is $2850\sim 3000\text{ cm}^{-1}$, through which the type of hydrate can be judged and the formation and decomposition of hydrate can be determined; the stretching vibration range of *O-H* bond is mainly in the range of $3000\sim 3800\text{ cm}^{-1}$. The formation of large and small cages in hydrates is mainly due to the presence of hydrogen bonds in structural water, and the stretching vibration of *O-H* bonds shifts to lower wave numbers when hydrogen bonds exist.

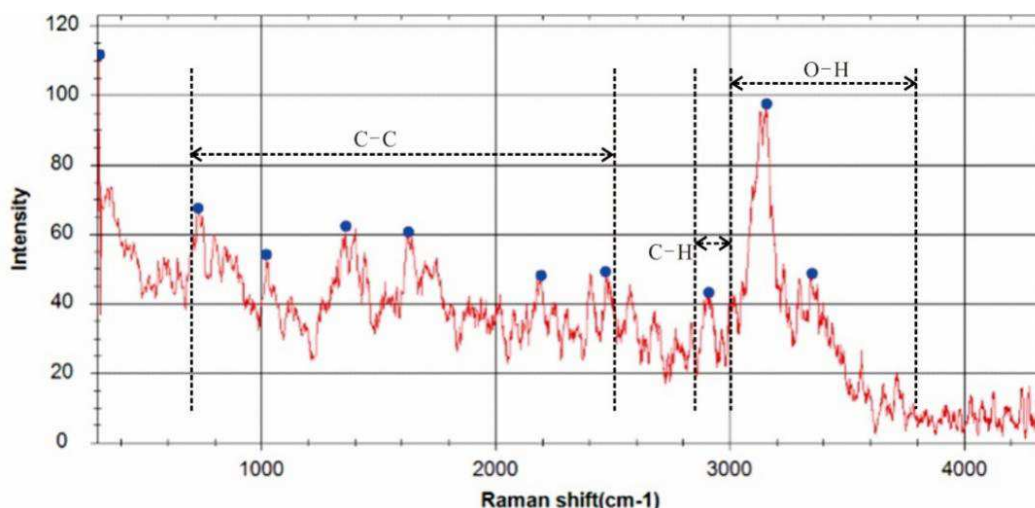


Figure 3. Raman spectrum of bonds in gas hydrate.

3.3. Analysis of Hydrate Decomposition Process

The decomposition process of natural gas hydrate was

measured by a laser Raman detector within a certain period of time, as shown in Figure 4. Under the conditions of normal temperature and pressure, the peaks of *C-H* bonds and *C-O*

bonds in the hydrate gradually became smaller with the increase of time and gradually disappear. The hydrogen bond energy in structural water also gradually decreases, and after a period of time, it becomes the Raman spectrum peak of liquid water. As the hydrate gradually decomposes at room temperature and pressure, the cage structure formed by structural water relying on hydrogen bonds disappears, the van der Waals force weakens, and the CH_4 molecules bound in the cage structure are released [26-28]. The released CH_4 molecules are in the same environment, without the constraints of large and small cages. It can be seen from the Raman spectrum that, the spectrum changes from a double peak to a single peak around 2910cm^{-1} . The O-H bond is finally converted into the O-H bond in liquid water after the

hydrogen bond energy gradually disappears. By recording the decomposition time of the hydrate at normal temperature and pressure, it can be seen that it takes about 30 minutes for the hydrate to dissociate at normal temperature and pressure. With the increase of time, through the Raman spectra of C-H bond and O-H bond energy change at 2914 cm^{-1} and 3210 cm^{-1} (Figure 5), it can be intuitively seen that hydrates are extremely easy to operate at room temperature and normal pressure. In the first 20 min of decomposition, the C-H bond peak of the hydrate is stronger at room temperature, and the overall trend is decreasing. Therefore, in the process of mining and transportation of hydrate, it is necessary to maintain a certain pressure and temperature all the time, so that it can be effectively exploited.

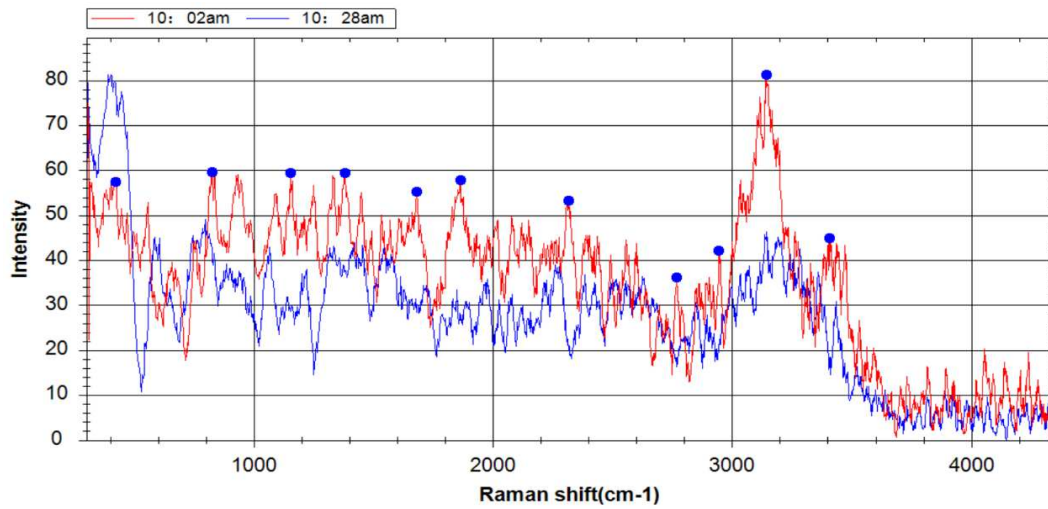


Figure 4. Raman spectrum of natural gas hydrate disappearing with time.

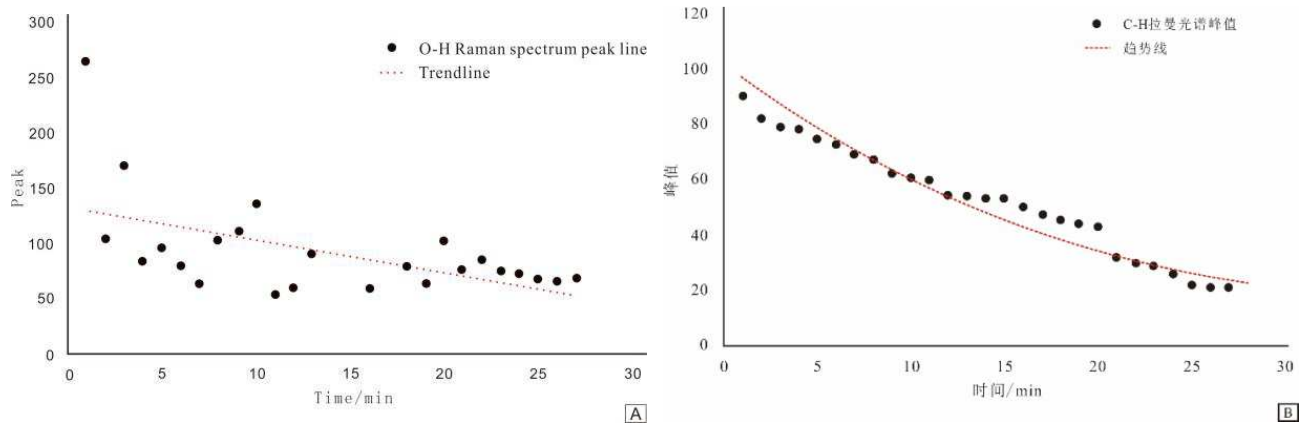


Figure 5. Changes of C-H bond and O-H bond energy with time.

A: O-H bond Raman peak value vs. time curve, the trend line formula is: $y = 102.46e^{-0.054x}$; B: C-H bond Raman peak value vs. time curve, trend line formula is: $y = -28761x + 131.45$.

4. Qualitative Identification of Natural Gas Hydrate

The principle of qualitative identification of hydrates is to match the measured Raman spectral data with the mineral

standard Raman spectral data in the database, so as to achieve qualitative identification of unknown hydrates. Therefore, qualitative identification should firstly establish a standard Raman database of minerals [29].

The wavelet transform method was used to identify the peaks of the Raman spectrum. Using wavelets with tight support in both time and frequency domains to decompose

the peaks of Raman spectra by wavelet, local time-frequency information can be obtained. By changing the wavelet scale, multi-resolution analysis of Raman peaks can be made [30], so that the information of the peaks in the Raman spectrum can be obtained more effectively. It can be seen from the wavelet coefficient oscillation diagram of the Raman

spectrum peak shown in Figure 6 that after connecting the local maxima of the wavelet spectrogram, the spectral peaks can be identified by searching the ridges in different wavelet coefficient matrices. Using the above method, a hydrate laser Raman spectral library was established under standard conditions.

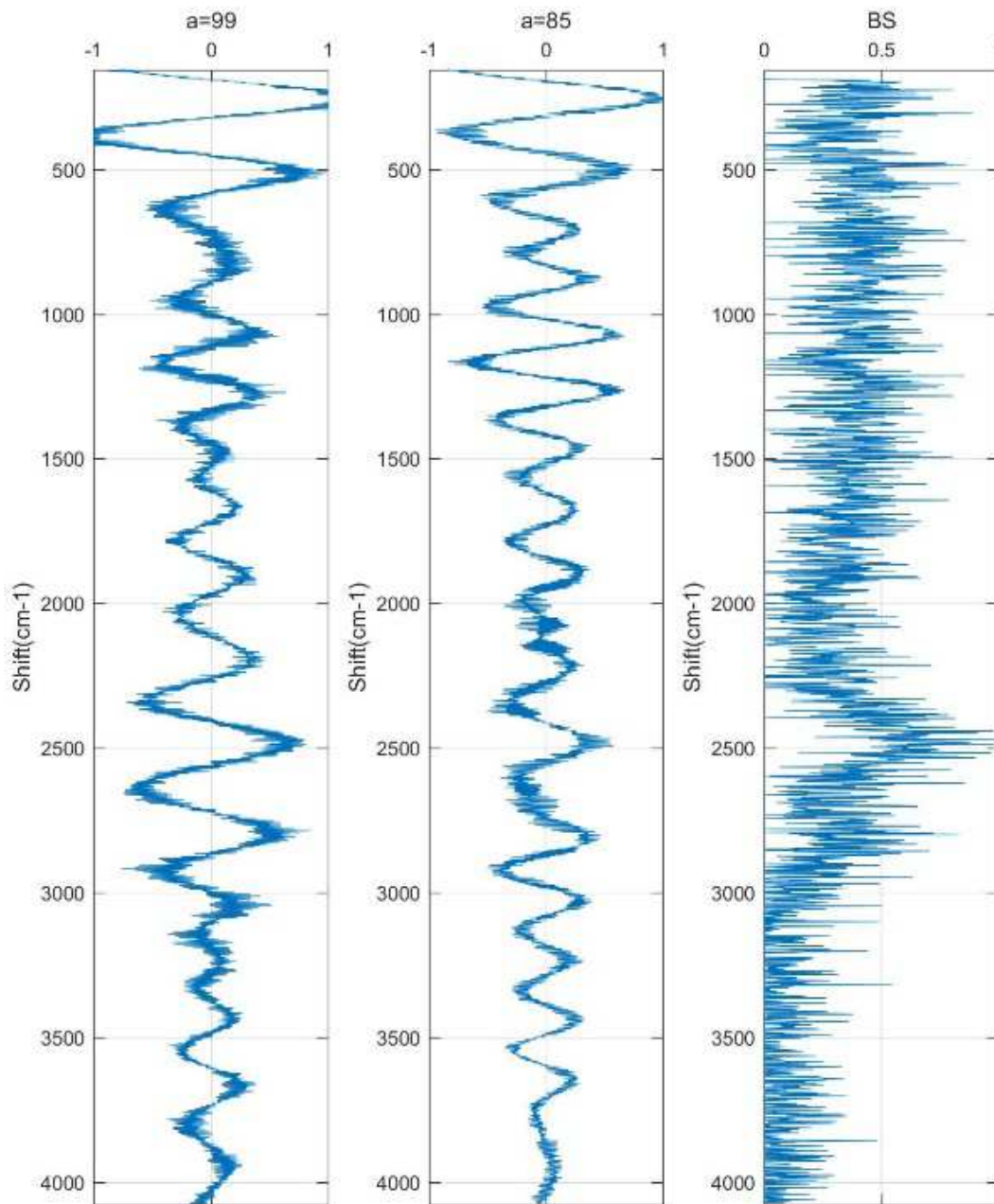


Figure 6. Oscillation diagram of wavelet coefficient of Raman spectrum peak.

The Raman spectra of laboratory-prepared hydrates after defluorescence treatment were compared using Raman spectroscopy analysis software (Figure 7). Due to the particularity of hydrates, the peak intervals corresponding to the three bond energies of *C-C* bond, *C-H* bond and *O-H* bond have been widely known. The problem of Raman spectrum analysis of substance species is transformed into the relationship between the wavenumber of characteristic peaks

of Raman fingerprint and substance species and content. According to this theory, the Raman characteristic peak wavenumber can be used as the judgment basis for qualitative analysis of substances. The hydrate analysis library established by Raman spectrum and wavelet analysis can be applied to the deep-sea combustible ice mining and pipeline transportation to quickly detect hydrates, reducing the influence of temperature and pressure on hydrates.

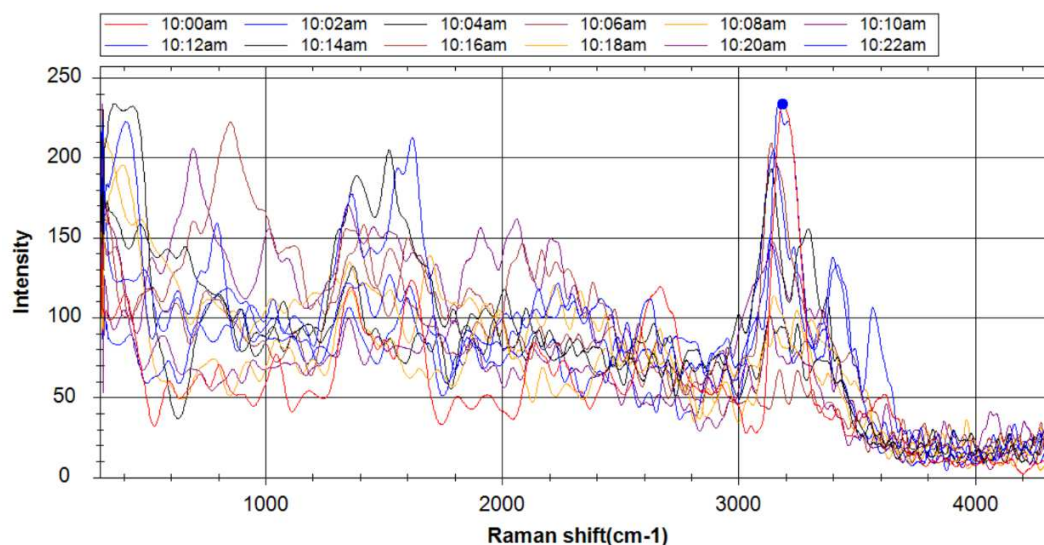


Figure 7. Comparison of Raman spectra of hydrates prepared in the laboratory at different times.

5. Conclusion

In this paper, a hydrate synthesis instrument is used in the laboratory to synthesize mixed gas hydrates, and the generated hydrates are detected and analyzed at room temperature. The structure type of hydrate was determined by the peak area ratio of Raman spectrum, and the hydrate analysis library was established by Raman spectrum construction and wavelet analysis, which realized the rapid detection of hydrate. The results show that the hydrate sample has a type II structure, the hydrate gradually decomposes at room temperature, the *C-H* bond energy gradually weakens, and the *C-H* bond energy is basically undetectable with the passage of time. Combined with the method of wavelet analysis, the peaks of Raman spectra can be effectively identified. Experiments show that laser Raman is a powerful means to determine the structure of natural gas hydrate, and the Raman spectroscopic analysis technology can detect natural gas hydrate in real time and in situ without destructive sample preparation. The application of laser Raman spectroscopy to the online detection of natural gas hydrate has theoretical basis and technical conditions, has operability and applicability, and has advantages and practicability different from other methods. It can be used in the field of detection while drilling, natural gas hydrate to provide technical support for methodological innovations and advancements in the field of mining and transportation. However, for the Raman spectroscopy detection of multi-component complex gas hydrates, it is difficult to distinguish various gases due to the overlapping peaks of different components in the *C-H* bond peak interval. Therefore, this method is also used in the study of complex gas mixed hydrates to be further in-depth. In order to deeply study the formation conditions and Raman spectral characteristics of hydrates in inclusions, and to make the research results more extensive, further research is needed on the formation of methane hydrates in salt-containing systems.

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