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# Raman characteristics of hydrocarbon and hydrocarbon inclusions

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The Raman spectrograms of hydrocarbon standard samples show that: (1) the Raman spectrogram of normal paraffin has very strong peaks of methyl and methylene (from 2700  $\text{cm}^{-1}$  to 2970  $\text{cm}^{-1}$ ); (2) branch methyl has the particular peak of 748 cm<sup>-1</sup> $\pm$ ; (3) six cyclic has the particular peak of 804 cm<sup>-1</sup> $\pm$ ; (4) phenyl has two particular peaks of 988 cm<sup>-1</sup>± and 3058 cm<sup>-1</sup>± and the 988 cm<sup>-1</sup>± peak is stronger than the 3058 cm<sup>-1</sup> $\pm$  peak; and (5) hexene has three alkenyl spectrum peaks of 1294 cm<sup>-1</sup> $\pm$ , 1635 cm<sup>-1</sup> $\pm$  and 2996 cm<sup>-1</sup>±, with the 1635 cm<sup>-1</sup>± peak being the strongest, showing that the number of carbon in hydrocarbon does not affect its Raman spectrogram, and the hydrocarbon molecular structure and base groups affect its Raman spectrogram, the same hydrocarbons (such as normal paraffin) have the same Raman spectrogram; the types (such as  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ ) and the content of hydrocarbon in oil inclusions are not estimated by their characteristic Raman peaks. According to the Raman spectrograms of hydrocarbon compositions, the Raman spectrogram of hydrocarbon inclusion can be divided into five types: saturated hydrocarbon Raman spectrogram, fluoresce Raman spectrogram, saturated hydrocarbon bitumen Raman spectrogram, bitumen Raman spectrogram, and ethane Raman spectrogram. And according to the characteristics of Raman spectrogram, hydrocarbon inclusions can be divided into five types: saturated hydrocarbon inclusion, less saturated hydrocarbon (oil or gas) inclusion, saturated hydrocarbon bitumen inclusion, bitumen inclusion, and methane water inclusion.

Raman, Raman spectrogram, oil, hydrocarbon inclusion

In 1928, C.V. Raman, an Indian physicist, discovered that there are other spectra with different frequency of incidence light and weak intensity besides some spectra having the same frequency of incidence light in dispersion. The spectrum with the same frequency is known as Rayleigh scattering and that with different frequency is called Raman effect. The Raman effect arose from the inelastic collision between the light and the molecule. The number, intensity and shape of the Raman spectrum are correlative with molecular vibration or base group vibration, i.e. the same base group, e.g. methyl in different hydrocarbons, has the same Raman spectrum.

Oil inclusions are oil and gas that are included in minerals. Many geologists have tested the compositions in inclusions with Raman, for example anions  $(SO_4^{2-},$ 

 $CO_3^{2-}$ ,  $HCO_3^{-}$ ,  $NO_3^{-}$ , etc.) in saltwater inclusions are successfully tested with Raman at freeze<sup>[1,2]</sup>. Previously, some geologists considered that the low carbon hydrocarbons (such as CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>6</sub>, etc.) of oil inclusions can be tested with Raman<sup>[3-6]</sup>. Usually there are not alkenes and alkynes (such as C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub> and C<sub>4</sub>H<sub>6</sub>) in oil and inclusions, because they are very soon deoxidized with hydrogen and become alkane or they are deoxidized with sulfurated hydrogen and become sulfurization hydrocarbon in sediment<sup>[7]</sup>. The authenticity of testing C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub> and C<sub>4</sub>H<sub>6</sub> in inclusions with Raman still

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needs to be further authenticated. In addition, there are methyls and methylenes in  $CH_4$ ,  $C_2H_6$  or  $C_3H_8$ , so their Raman spectrograms are the same in theory. There are a few low carbon hydrocarbons in oil, and high carbon hydrocarbons have the same base groups as low carbon hydrocarbons. And how can the low carbon hydrocarbon be tested from so many hydrocarbon mixtures? By many tests of oil inclusions with Raman, we find that the Raman spectrograms of some oil inclusions are characteristic of fluorescence width peaks and they have similar spectrum peaks, but not each oil inclusion has a particular Raman spectrogram. Theoretically many kinds of oil inclusions formed at different ages and in different areas in nature have a particular Raman spectrogram.

# 1 Raman spectrogram of hydrocarbon standard samples

#### 1.1 Experimental conditions

All Raman spectrograms in this paper were tested by  $514.32 \ \mu m$  laser of JY-1000 Raman at normal temperature and at normal pressure. And the test time must be shorter (for instance, 1s), because hydrocarbons can be disassembled at a long time. For convenience of contrasting with all samples' Raman spectrograms, all samples were tested in these conditions. To ensure the accuracy of samples' Raman spectra, we proofread the Raman instrument with silicon before testing.

#### 1.2 Raman spectrogram of normal paraffin

By testing standard hydrocarbon samples (made by China Measure Academy of Sciences), we found that the Raman spectrogram of normal paraffin has characteristic peaks of 2870.48-2872.96 cm<sup>-1</sup> and 2933.88-2936.35 cm<sup>-1</sup> (counts per Raman shift)<sup>[8]</sup>. Different normal paraffins have the same Raman spectrogram (Figure 1), because their molecules are composed of methyl  $(-CH_3)$ and methylene  $(-CH_2-)$  and their molecular structures determine their Raman spectrograms. Normal pentane, normal hexane and normal heptane have different numbers of carbon in their molecules. They have the same molecular structures, so they have the same Raman spectrogram (Figure 1). Because high carbon normal pentane has more base groups than low carbon normal pentane, the peak of high carbon normal pentane is stronger than that of low carbon normal pentane under the same test condition.

The characteristics of isoparaffin Raman spectrogram have been described in *Raman Characteristics for Saturated Hydrocarbons*<sup>[8]</sup>. These cases in Figure 2 further show that the Raman spectrogram of all isoparaffins has a characteristic peak of 749.32 – 762.833 cm<sup>-1</sup>; and that peak of 2911.61–2913.19 cm<sup>-1</sup> of isoparaffin is stronger than that of normal paraffin. The 2911 cm<sup>-1</sup>± peak is regarded as the characteristic peak of methane. In mix hydrocarbons or oil inclusions, the 2911.61– 2913.19 cm<sup>-1</sup> peak is the characteristic Raman peak of methylene, but not that of methane. In methane and inorganic compound, the 2905–2921 cm<sup>-1</sup> Raman spectrum peak is of methane.



**Figure 1** The Raman spectrogram of normal paraffin. a, n-pentane  $(C_{5}H_{12})$ ; b, n-hexane  $(C_{6}H_{14})$ ; c, n-heptane  $(C_{7}H_{16})$ 



**Figure 2** The Raman spectrogram of isoparaffin. a, Isopentane  $(C_5H_{12})$ ; b, isooctane  $(C_8H_{18})$ ; c, mix paraffin  $(\Sigma C_{13-n})$ .

### **1.3** Raman spectrogram of hexene, cyclohexane and benzene

Figure 3 shows the Raman spectrogram of hydrocarbon with six carbons. Compared with normal paraffin (Fig-

ure 3a), not only 3058 cm<sup>-1</sup> $\pm$  peak, but also 988 cm<sup>-1</sup> $\pm$  peak (Figure 3b) appear in the Raman spectrogram, i.e. benzene has two characteristic peaks of 988 cm<sup>-1</sup> $\pm$  and 3058 cm<sup>-1</sup> $\pm$ , with the 988 cm<sup>-1</sup> $\pm$  peak being stronger.

The hexene has three Raman spectrum peaks of 1294 cm<sup>-1</sup> $\pm$ , 1635 cm<sup>-1</sup> $\pm$  and 2996 cm<sup>-1</sup> $\pm$  (Figure 3c), with the 1635 cm<sup>-1</sup> $\pm$  peak being the strongest. The methylene peak (2914 cm<sup>-1</sup> $\pm$ ) of hexene is stronger than that of hexane. Previously the characteristic peaks of C<sub>2</sub>H<sub>4</sub> or C<sub>3</sub>H<sub>6</sub> were regarded as 3013-3020 cm<sup>-1</sup> or 1292-1297 cm<sup>-1</sup>. According to Raman spectrum characteristics of hexane, the 3013-3020 cm<sup>-1</sup> and 1292-1297 cm<sup>-1</sup> peaks are possibly one of three alkenyl Raman spectum peaks.

The six cyclic base characteristic peak of cyclohexane is a 1635.6 cm<sup>-1</sup> peak. The methyl characteristic peak (2855 cm<sup>-1</sup> $\pm$ ) of cyclohexane is smaller 16 cm<sup>-1</sup> than that (2871 cm<sup>-1</sup> $\pm$ ) of hexane.

These characteristic peaks of phenyl, alkenyl or six cyclic base are low counts Raman shift. They all have very strong Raman effect at  $2700-2970 \text{ cm}^{-1}$ , but their characteristic peak's count of methyl or methylene maybe changes.

Analyzing standard samples showed that the Raman spectrogram is not related to the carbon number of hydrocarbon, but to hydrocarbon molecular structure and base group; the same hydrocarbons as normal paraffins have the same Raman spectrogram; the kind (e.g.  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ ) and relative content of hydrocarbon in oil inclusions are not estimated only by their characteristic Raman peaks.



**Figure 3** The Raman spectrogram of hydrocarbon with six carbons. a, Hexane  $(C_6H_{14})$ ; b, benzene  $(C_6H_6)$ ; c, hexene  $(C_6H_{12})$ ; d, cyclohexane  $(C_6H_{12})$ 

# 2 The general characteristics of Raman spectrum of oil compositions

Oil compositions can be divided into saturated hydro-

carbon, aromatic hydrocarbon, non-hydrocarbon compound and bitumen. The four compositions have particular Raman spectrum characteristics (Figure 4)



Figure 4 The Raman spectrogram of four compositions in oil. a, Aromatic hydrocarbon; b, bitumen; c, non-hydrocarbon compound; d, saturated hydrocarbon.

### 2.1 Raman spectrum characteristics of saturated compositions

Saturated hydrocarbon has very good Raman spectra (Figures 1-4) and the Raman spectrum characteristics of saturated compositions are:

(1) There are very strong spectrum peaks at  $2700-2970 \text{ cm}^{-1}$ (Figure 4a). The different saturated compositions have the different Raman spectra: the methyl special Raman peak (2872 cm<sup>-1</sup>±) is the strongest at normal paraffin; the methylene special Raman peak (2911 cm<sup>-1</sup>±) is the strongest at isoparaffin ; and the methylene special Raman peak (2857 cm<sup>-1</sup>±) is the strongest at cycloparaffin.

(2) The particular peak of branch methyl is 748  $\text{cm}^{-1}\pm$ .

(3) The particular peak of six cyclic is 804 cm<sup>-1±.</sup>

(4) Different saturated hydrocarbons have different numbers of carbon, but if they have the same molecular structure, they have the same Raman spectrogram.

The saturated hydrocarbon is composed of a few base groups such as methyl, methylene, branch methyl and naphthene. The Raman spectrogram of saturated hydrocarbons is rested with these base groups. There are infinite base groups and finite Raman spectrograms, so we can unscramble useful information from these finite Raman spectrograms. Figure 1 shows that different normal hydrocarbons have the same base groups, so they have the same Raman spectrogram. And Figure 2 shows that different isoparaffins have the same base groups, so they have the same Raman spectrogram. These two examples have proved that infinite saturated hydrocarbons could have finite Raman spectrograms.

The saturated hydrocarbon is a mixture of isoparaffin and cycloparaffin. Thus the kind and content of hydrocarbon in inclusions cannot be estimated by their characteristic Raman peaks.

#### 2.2 Raman spectrum characteristics of bitumen

Bitumen has very big molecule and many base groups. By many tests, although fluorescence wide peaks have different wave numbers, all bitumen Raman spectrograms are the same, that is, there are two steady peaks  $(1360 \text{ cm}^{-1} \pm \text{ and } 1620 \text{ cm}^{-1} \pm)$  at the Raman spectrogram of bitumen (Figure 4b), especially the 1620 cm<sup>-1</sup> $\pm$  peak is stronger. These two peaks can be seen as characteristic Raman effect of bitumen.

## 2.3 Raman spectrum characteristics of aromatic hydrocarbon

Aromatic hydrocarbon molecule has not only alkane branch cyclic, but also aromatic ring. Theoretically, there are very abundant peaks in their Raman spectrogram, and two Raman spectrum characteristic peaks of phenyl (988 cm<sup>-1</sup> $\pm$ , 3058 cm<sup>-1</sup> $\pm$ ) are representative of aromatic hydrocarbon. Because aromatic hydrocarbon has strong fluorescence, there is one  $(3000 \text{ cm}^{-1} \pm)$  or two (2000 cm<sup>-1</sup> $\pm$  and 3000 cm<sup>-1</sup> $\pm$ ) fluorescence wide peaks at their Raman spectrograms. The Raman spectrogram of aromatic hydrocarbon must be characteristic of about three fluorescence wide peaks. Because aromatic hydrocarbon is very complex, fluorescence wide peaks at their Raman spectrogram have different wavenumbers. And because aromatic hydrocarbon exists in oil inclusions, many Raman spectrograms of oil inclusions are fluorescence wide peaks, instead of sharp peaks. If there are a certain number of aromatic hydrocarbons in oil inclusions, the Raman spectrum must appear as fluorescence wide peaks. Inversely, the oil inclusions of the Raman spectrum with fluorescence wide peaks certainly have many aromatic hydrocarbons.

#### 2.4 Raman spectrum characteristics of non-hydrocarbon compound

Non-hydrocarbon compound in oil is mainly hydrocarbon with O, S, N, halogen impurity in its molecule. The chemical bonds of O, S, N, halogen combining with CH are very weak. The halogen-carbons have some weak Raman spectrum peaks within  $400-700 \text{ cm}^{-1[9,10]}$ . The S—H has some weak Raman spectrum peaks between  $2590-2560 \text{ cm}^{-1}$ , the S–C has those between 600-~760 cm<sup>-1</sup>, the C=N has those between  $1600-1700 \text{ cm}^{-1}$ ; and the C=O has those between  $1700-1800 \text{ cm}^{-1}$ . Because these peaks are very weak, the Raman spectrograms of non-hydrocarbon show as fluorescence wide peaks.

Through analysis of Raman spectrum of aromatic hydrocarbon and non-hydrocarbon, we can find that the fluorescence effect of aromatic hydrocarbon and nonhydrocarbon is the biggest barrier to testing Raman characteristics of hydrocarbon inclusions.

There are no fluorescence wide peaks in the Raman spectrum of saturated hydrocarbon and benzene. But there are fluorescence wide peaks in the Raman spectrum of oil compositions except for saturated hydrocarbon. There are many big chain aromatic base groups in aromatic hydrocarbon and non-hydrocarbon compound, so we assume that the fluorescence effect results from big chain aromatic base groups. Because of strong fluorescence effect (Figure 4a, c), it is almost impossible to test aromatic hydrocarbon and non-hydrocarbon compound with Raman.

# 3 Raman spectrum characteristics of oil inclusions

There are many kinds of hydrocarbon inclusions in nature. According to inclusion's state oil inclusions can be classified as liquid oil inclusion, gas oil inclusion, gas-liquid oil inclusion. And according to oil inclusion's color and fluorescence characteristics, oil inclusions can be classified as heavy oil inclusion, medium oil inclusion, light oil inclusion, condensate gas inclusion, wet gas inclusion and dry gas inclusion<sup>[11]</sup>. As yet there is no classification of hydrocarbon inclusion component, because of not effectively analyzing available components of oil inclusions. In this paper, according to the Raman characteristics and the components of oil inclusions, we have classified the Raman spectrogram of oil inclusions as well as oil inclusions.

Due to the complexity and the same base groups of oil inclusions, it is difficult to estimate hydrocarbon kind of oil inclusions and their content. Oil inclusions are composed of saturated hydrocarbon, aromatic hydrocarbon, non-hydrocarbon compound and bitumen, which affect the Raman spectrogram of oil inclusions. Although the four components of oil have complex molecule, they have common characteristics. From the above analysis we realized that saturated hydrocarbon has finite base groups and good Raman spectra without fluorescence effect. There are always two characteristic peaks in the Raman spectrogram of bitumen; the Raman spectrograms of aromatic hydrocarbon and non-hydrocarbon compounds are characteristic of fluorescence wide peaks. So according to the overall characteristics of Raman spectrograms, we can analyze the contents of saturated hydrocarbon, bitumen and aromatic hydrocarbon in oil inclusions.

Based on the test of some 1000 oil inclusions and according to the Raman spectrogram of compositions in oil, we divided the Raman spectrogram of hydrocarbon inclusions into five types.

#### 3.1 Saturated hydrocarbon Raman spectrogram

Because there are many aromatic hydrocarbons and non-hydrocarbons in oil inclusions, fluorescence effect is the most obstructive to testing the inclusion's Raman spectra. By testing many samples of oil inclusions we find that the Raman spectrograms of some inclusions are the same Raman spectrogram of saturated hydrocarbon (Figures 5 and 6) and we think that many saturated hydrocarbons exist in these oil inclusions. Very strong Raman spectrum peaks appear between 2700 cm<sup>-1</sup> to 2970 cm<sup>-1</sup>, which are the perfect Raman spectrogram which resembles saturated hydrocarbon Raman spectrogram. It shows that these inclusions have most saturated hydrocarbon composition. So the Raman spectrogram of these inclusions can be named saturated hydrocarbon Raman spectrogram.

Generally speaking, the saturated hydrocarbon Raman spectrogram has the following characteristics: (1) these saturated hydrocarbon Raman spectrogram is not affected by inclusion color (Figure 6a, b, c) and state (e.g. gas in Figure 5, liquid in Figure 6); however, the colorless oil inclusions more easily have oil or gas inclusions of saturated hydrocarbon (Figures 5e and 7a); (2) the Raman spectrogram of saturated hydrocarbon oil inclusions may be like that of saturated hydrocarbon gas inclusions, e.g. black oil inclusion at Mabei 8 well in the Qinghai oil field (Figure 5b) and black gas inclusion at Luojia 6 well in the Sichuan Basin (Figures 6e and 7b); and (3) two different hydrocarbon inclusions have the same Raman spectrogram, e.g. sandy beige oil inclusion at Mandong 1 well in the Tarim Basin (Figure 6a) and black oil inclusion at Mabei 8 well in the Qinghai oil field (Figure 5b).



**Figure 5** The Raman spectrogram of saturated hydrocarbon oil inclusion. a, Sandy beige oil inclusion at Mandong 1 well, Tarim Basin; b, black oil inclusion at Mabei 8 well, Qinghai oil field; c, colorless oil inclusion at An 71 well, Liaohe oil field; d, yellow gray oil inclusion at Sheng 8 well, Liaohe oil field; e, sandy beige oil inclusion at Tazhong 117, Tarim Basin; f, colorless oil inclusion at Xiang 3 well, Tarim Basin; g, colorless oil inclusion at Dina 201 well, Tarim Basin.



**Figure 6** The Raman spectrogram of saturated hydrocarbon gas inclusion. a, Black gas inclusion at Hade 4 well, Tarim Basin; b, black gas inclusion at Chongshen 2 well, Sichuan Basin; c, black gas inclusion at Hei 2 well, Sichuan Basin; d, black gas inclusion at Muo 24 well, Sichuan Basin; e, black oil inclusion at Luojia 6 well, Sichuan Basin.

**Figure 7** Kinds of oil inclusions. a, Beige oil inclusion at Tazhong 117 in the Tarim Basin; b, black oil inclusion at Luojia 6 well in the Sichuan Basin; c, brown gas-oil inclusion from dolomitic gangue at Yingdong 2 well, in the Tarim Basin; d, gas inclusion at Mandong 1 wellin the Tarim Basin; e, brown black bitumen inclusion from dolomitic gangue at Yingdong 2 well in the Tarim Basin; f, beige oil inclusion at Tazhong 117 in the Tarim Basin, at plane polarized light; g, beige oil inclusion at Tazhong 117, in the Tarim Basin, at purple fluorescence.

From these Raman spectrograms of saturated hydrocarbon we can identify methyl, methylene, cyclohexane, alkenyl branch, bitumen, etc. Suppose the 1620 cm<sup>-1</sup> peak stands for bitumen in oil inclusion (symbol A), the 988 cm<sup>-1</sup> phenyl peak stands for aromatic hydrocarbon in oil inclusion (symbol B), the sum of C-S S-H C=N C=O, etc. peaks stands for non-hydrocarbon compound of oil inclusion (symbol C) and [(methyl + methylene)-(A+B+C)] peaks stand for saturated hydrocarbon of oil inclusion (symbol  $\Sigma$ ). According to the characteristics of the Raman spectrogram, A, B, C and  $\Sigma$ , and (A+B+C)/ $\Sigma$ ratio, the period, origin and maturity of oil inclusions can be identified.

### 3.2 Saturated hydrocarbon+bitumen Raman spectrogram

A pair of peaks  $(1397 \text{ cm}^{-1} \pm \text{ and } 1614 \text{ cm}^{-1} \pm)$  in the Raman spectrograms of some bitumen inclusions have a very strong Raman spectrum peak between 2700-2970 cm<sup>-1</sup> (Figures 8 and 9). So these inclusion Raman spectrograms can be named saturated hydrocarbon + bitumen Raman spectrogram. Sometimes the black and brown oil inclusions are shown as the saturated hydrocarbon bitumen Raman spectrogram (Figure 7c), showing that the main composition is dominated by saturated hydrocarbon bitumen in clusions with a little number of bitumen. So these inclusions can be named saturated hydrocarbon bitumen oil inclusion (Figure 8). Some black gas inclusions have the features of the saturated hydrocarbon bitumen Raman spectrogram (Figures 7d and 9). Gas inclusions have often methane and low carbon hydrocarbon hydrocarbon hydrocarbon hydrocarbon hydrocarbon hydrocarbon hydrocarbon hydrocarbon bitumen Raman spectrogram (Figures 7d and 9).

bon compound. The bitumen Raman spectrum peaks show that there are some bitumen in gas inclusions. The body wall of the gas inclusion is often black for bitumen maybe adhere to inclusion walls. Thereby these inclusions can be named saturated hydrocarbon bitumen gas inclusions (Figure 9). Because the content of bitumen in inclusions varies, the intensity of bitumen Raman peaks in pair (1397 cm<sup>-1</sup> $\pm$  and 1614 cm<sup>-1</sup> $\pm$ ) also varies, and there is a positive correlation between both.



**Figure 8** The Raman spectrogram of saturated hydrocarbon bitumen oil inclusion. a, Brown oil inclusion from calcite at Tazhong 45 well, Tarim Basin; b, black oil inclusion from Carboniferous, Tarim Basin; c, brown gas-oil inclusion from dolomitic gangue at Yingdong 2 well, Tarim Basin; d, brown gas-oil inclusion from dolomitic gangue at Yingdong 2 well, Tarim Basin; e, brown gas-oil inclusion from calcite at Tazhong 45 well, Tarim Basin; e, brown gas-oil inclusion from calcite at Tazhong 45 well, Tarim Basin.



**Figure 9** The Raman spectrogram of saturated hydrocarbon bitumen gas inclusion. a, Gas inclusion at G43 well, Sichuan basin; b, gas inclusion at Du 4 well, Sichuan basin; c, gas inclusion at Muo 24 well, Sichuan basin; d, gas inclusion at Mandong 1 well, Tarim Basin.

#### 3.3 Bitumen Raman spectrogram

A pair of bitumen peaks (1397 cm<sup>-1</sup>± and 1614 cm<sup>-1</sup>±) appearing in the Raman spectrograms of some inclusions is the most often seen Raman spectrogram in bitumen in open system (Figure 10b), as well as in bitumen inclusions from which light hydrocarbon moves out (Figures 7e and 10). Some of these spectrograms have weak peaks from 2970 cm<sup>-1</sup>± to 3200 cm<sup>-1</sup>±, which are Raman effect of methyl and methylene in bitumen. These hydrocarbon inclusions with the bitumen Raman spectrogram can be named bitumen inclusion.



**Figure 10** The Raman Spectrogram of bitumen and bitumen inclusion. a, Black bitumen inclusion at Du 5 well, Sichuan basin; b, bitumen at Yingdong 2 well, Tarim Basin; c, black bitumen inclusion from dolomitic gangue at Yingdong 2 well in, Tarim Basin; d, brown-black bitumen inclusion at Lunnan 63 wellin the Tarim Basin; e, black bitumen inclusion at Du 24 well in the Sichuan Basin.



**Figure 11** The Raman spectrogram of less saturated hydrocarbon oil inclusion. a, Black gas inclusion at Gan 174 well in the Jilin oil field; b, black gas inclusion from ratoffkite at Tazhong 45 well in the Tarim Basin; c, black oil inclusion at Lungu 38 well, in the Tarim Basin; d, liquid state of sandy beige gas-oil inclusion at Gan 181 well in the Jilin oil field; e, gaseity of sandy beige gas-oil inclusion at Gan 181 well, in the Jilin oil field.

In addition, weak 2250 cm<sup>-1</sup>± peak often appears in the Raman spectrogram of hydrocarbon inclusions (Figures 5–10). The numbers of Raman peaks are constant. In hydrocarbon  $-SiH_2$  (2149 cm<sup>-1</sup>±), P–OH (2080– 2350 cm<sup>-1</sup>) and  $-NH_3$  (2000–2800 cm<sup>-1</sup>) have Raman effect at about 2250 cm<sup>-1</sup>. This peak of the Raman spectrogram has not been found in the hydrocarbon standard sample, so this peak probably is the result of impurity group.

Besides, there are often 2250 cm<sup>-1</sup> $\pm$  peak in the Raman spectrogram of oil inclusions. The peak has steady wavenumbers and a sharp top. The peak is not found in the Raman spectrum of standard hydrocarbon samples and oil four compositions. There is not this peak in the Raman spectrum of quartz, calcite and glass in which there are inclusions. So we conjecture that this peak is a Raman spectrum characteristic of inorganic base group such as -CN base<sup>[9,10]</sup>.

#### 3.4 Fluorescence Raman spectrogram

Most of hydrocarbon inclusions, with one  $(3000 \text{ cm}^{-1}\pm)$  or two  $(2000 \text{ cm}^{-1}\pm \text{ and } 3000 \text{ cm}^{-1}\pm)$  fluorescence wide peaks (Figure 11), have this Raman effect, which appears not only in fluorescence oil inclusions (Figures 7f, g and 11d), but also in non-fluorescence oil or gas inclusions (Figure 11c or Figure 11a, b). There are not only aromatic hydrocarbon but also non-hydrocarbon compound and bitumen in hydrocarbon inclusions. Because non-hydrocarbon compound and bitumen contain phenyl,

they make fluorescence effect at the Raman spectrogram. These hydrocarbon inclusions contain much aromatic hydrocarbon, non-hydrocarbon compounds, bitumen and a few saturated hydrocarbons, so these inclusions can be called less saturated hydrocarbon oil or gas inclusion.

In a word, the fluorescence Raman spectrogram does not have a sharp peak, so it is difficult to identify an effective peak from this spectrogram and analyze the information of inclusion's composition. By experiment we found that most hydrocarbon inclusions had fluorescence Raman spectrograms, so it can be seen that it is very limited to analyze the inclusion composition with LRM.



Figure 12 Methane Raman spectrogram.

#### 3.5 Methane Raman spectrogram

The methane Raman spectrogram with a clear 2911  $\text{cm}^{-1}\pm$  peak (Figure 12) has been obtained from gaseity in inclusions of two-phase saltwater gas. The gaseity of saltwater inclusion is dominated by methane, with a lit-

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tle inorganic compound. So this inclusion can be called methane saltwater inclusion.

#### 4 Conclusions

Based on many Raman tests of some standard samples, the Raman characteristics of each alkyl and hydrocarbon and the Raman spectrum characteristics of oil four compositions have been summarized. According to the Raman characteristics of hydrocarbon inclusions, the Raman spectrogram of hydrocarbon inclusions can be divided into five types: saturated hydrocarbon Raman spectrogram, fluorescence Raman spectrogram, saturated hydrocarbon bitumen Raman spectrogram, bitumen Raman spectrogram, and ethane Raman spectro-gram. Correspondingly, hydrocarbon inclusions can be divided into five types: saturated hydrocarbon oil inclusion, less saturated hydrocarbon (oil or gas) inclusion, saturated hydrocarbon bitumen oil inclusion, bitumen inclusion, and methane water inclusion.

In a word, the Raman spectrograms of hydrocarbon inclusions have some guiding meanings, although the fluorescence of inclusion influences the identification of the Raman spectrograms, the Raman spectrograms have the similar feature due to the same alkyl in different hydrocarbons, and hydrocarbon types cannot be identified due to the complexity of hydrocarbon compositions and comparability of different alkyls.

At present, it is inaccurate to analyze the amount of low carbon hydrocarbon with LRM. But according to the general Raman characteristics, types of hydrocarbon inclusions can be qualitatively analyzed, and the period, origin and maturity of hydrocarbon inclusions can be further identified.

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