Talanta 119 (2014) 105–110

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

# Concept and properties of an infrared hybrid single-beam spectrum and its application to eliminate solvent bands and other background interferences

Yujing Chen [a], Hai-Shui Wang [a,*], Yusuke Morisawa [b], Yukihiro Ozaki [c]

[a] *School of Chemistry and Chemical Engineering, The Key Laboratory of Fuel Cell Technology of Guangdong Province, South China University of Technology, Guangzhou 510640, China*
[b] *Department of Chemistry, School of Science and Engineering, Kinki University, Osaka 577-8502, Japan*
[c] *Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, 2-1 Gukuen, Sanda, Hyogo 669-1337, Japan*

ARTICLE INFO

*Article history:*
Received 26 April 2013
Received in revised form
24 October 2013
Accepted 25 October 2013
Available online 1 November 2013

*Keywords:*
Infrared spectroscopy
Hybrid single-beam spectrum
Spectral distortion
Solvent interference
Background elimination

ABSTRACT

For infrared (IR) spectral measurements, if a quality single-beam background spectrum with desired intensity could be obtained, the contributions from solvent and other background components could be completely suppressed and their bands would not appear in a final transmittance/absorbance spectrum. In order to achieve this ideal but difficult goal, the concept of hybrid single-beam spectrum is introduced in this paper. The hybrid single-beam spectrum ($\phi_h$) is defined as a mixture of two single-beam spectra ($\phi_{b1}$ and $\phi_{b2}$) of the same sample but with different pathlengths ($b_1$ and $b_2$), namely, $\phi_h = \alpha\phi_{b1} + (1-\alpha)\phi_{b2}$, where $\alpha$ ($0 \le \alpha \le 1$) is the component factor. The properties of the hybrid spectrum have been investigated. Under conditions of $b_2 > b_1 \ge 0.7b_2$ and $A_{max} \le 0.60$ ($A_{max}$ is the maximum absorbance of $b_2$ sample in the spectral range of interest), all the synthesized hybrid spectra are free from significant distortion regardless of the component factor. Therefore, the hybrid single-beam spectrum with desired intensity can be easily obtained simply by choosing an appropriate component factor. The proposed methodology has been demonstrated experimentally by the complete removal of the interference from the atmospheric water vapor and solvent.

## 1. Introduction

Fourier transform infrared (FT-IR) spectroscopy has tremendous applicability and versatility in a variety of fields such as physics, chemistry, environmental, material, biomedical and pharmaceutical sciences [1–7]. FT-IR spectroscopy is also a highly sensitive analytical technique that can detect even very small amounts of samples and ultrathin films [8,9]. By the use of various sampling accessories [10–12], an IR spectrometer can accept a wide range of sample types such as gases, liquids, solids, crystals and films. In the case of liquids or solutions, a wide variety of commercially available liquid cells with a pathlength ranging from a few micrometers to several millimeters can be used.

In order to acquire a high quality IR spectrum of a solution, an analyst must take into account the noise from the surrounding media, namely solvent and other background components. Unfortunately, every solvent has its own IR spectrum, and none of solvents is transparent through the entire mid IR region. Several methods have thus far been proposed to minimize the interference from solvent and other background absorption [12–20].

The straight way to minimize the solvent interference is to find a solvent that is relatively IR-transparent within the spectral region of interest. The commonly used solvents are carbon tetrachloride and carbon disulfide, which are, however, quite toxic and must be handled with great caution [12].

Secondly, solvent bands may be removed by subtracting the solvent spectrum from the sample solution spectrum [12–15]. Griffiths pointed out that the closer the value of the scaling factor to unity, the better the subtraction [12]. For example, the spectral subtraction has been extensively applied to eliminate water interference from an aqueous solution spectrum especially in an attenuated total reflectance (ATR) measurement [16–18].

The third method is to prepare an appropriate background sample. If the concentrations and pathlengths of the background components are the same when the background and sample spectra are obtained, the contributions to the final transmittance or absorbance spectrum from the background components will cancel out exactly and the bands due to the background components would not appear. However, it would be exceedingly difficult to prepare such a quality background sample with desired pathlength in practice [2,19,20].

---

[*] Corresponding author. Tel.: +86 20 2223 6516.
*E-mail address:* wanghsh@scut.edu.cn (H.-S. Wang).

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.10.058

To obtain the compensation of solvent bands, one may select a variable pathlength liquid cell. The pathlength can be continuously adjusted from 0.05 mm to 5 mm and reproduced within 0.001 mm (1 μm). However, the applications of the variable pathlength cells, which are available commercially, are limited because they are costly and are difficult to clean. Another problem with a variable pathlength liquid cell is that the pathlength control down to a submicrometer scale becomes very difficult because of the screw mechanism.

All these existing methods suffer from certain limitations in obtaining a quality spectrum without interference of background components. In this paper, we propose a new method to achieve the background elimination, and introduce a new concept of IR hybrid single-beam spectrum. The unique advantage of the hybrid spectrum is that its intensity can be easily adjusted by a component factor, and thus a desired hybrid single-beam background spectrum can be easily obtained. As a result, solvent bands and other background interferences will be eliminated completely. Moreover, because of the nature of the single-beam spectrum, this new method can be applied to spectral measurement with any ordinate scale including transmittance, reflectance, absorbance, etc.

## 2. Theoretical consideration

### 2.1. The concept of the hybrid spectrum

It is well known that an IR spectral measurement requires a background spectrum as a reference. In the case of a background spectrum without any background sample present, the intensity of a single-beam background spectrum at any wavenumber ($\nu$) is defined as $\phi_0$.

In most cases a background sample is involved in the measurement of a background spectrum, as water vapor or solvent. If absorption coefficient ($K$) of the background sample at a wavenumber ($\nu$) is known, the intensity of the transient single-beam background spectrum resulting from the background sample with a pathlength (thickness) of $b$, designated as $\phi_{tr}$, can be represented as

$$\phi_{tr} = \phi_0 e^{-Kb} \tag{1}$$

The definition of a hybrid single-beam spectrum is given below. If $N_1$ scans for a sample with a thickness of $b_1$ are followed by $N_2$ scans for the same sample but with a different thickness of $b_2$ (in this paper, always assuming that $b_2 \geq b_1$), the final accumulated single-beam spectrum should be their average when an IR spectrometer has completed the total number ($N_1+N_2$) of scans.

$$\phi_{final} = \frac{N_1\phi_0 e^{-Kb_1} + N_2\phi_0 e^{-Kb_2}}{N_1+N_2} = \frac{N_1}{N_1+N_2}\phi_0 e^{-Kb_1} + \frac{N_2}{N_1+N_2}\phi_0 e^{-Kb_2} \tag{2}$$

Clearly, $\phi_{final}$ contains spectral information from both $b_1$ and $b_2$ samples (hereafter called hybrid spectrum $\phi_h$).

Generally, the intensity of a hybrid single-beam spectrum at any wavenumber ($\nu$) can be defined as

$$\phi_h = \alpha\phi_0 e^{-Kb_1} + (1-\alpha)\phi_0 e^{-Kb_2} (0 \leq \alpha \leq 1) \tag{3}$$

where, $\phi_0 e^{-Kb_1}$ and $\phi_0 e^{-Kb_2}$ are the two single-beam spectra of the same sample with different pathlengths. Alpha ($\alpha$) is a component factor, representing the contribution of $\phi_0 e^{-Kb_1}$ in the hybrid spectrum. In Eq. (3), $\alpha$ may take an arbitrary value between zero and unity, and thus, the total number of hybrid spectra can be infinite.

In solutions, an infrared hybrid single-beam spectrum can be defined as a mixture of two single-beam spectra from two solutions with the same ingredients but at different concentrations. The intensity of the hybrid spectrum of the related component (including solvent) at any wavenumber ($\nu$) is given as

$$\phi_h = \alpha\phi_0 e^{-abc_1} + (1-\alpha)\phi_0 e^{-abc_2} \quad (0 \leq \alpha \leq 1) \tag{4}$$

Here, $c_1$ and $c_2$ are the concentrations of the related component, $b$ is the pathlength, and $a$ is the absorptivity of the component involved.

### 2.2. The properties of the hybrid spectrum

As stated above, a hybrid single-beam spectrum can be obtained by mixing two spectra, which are of the same sample but of different pathlengths ($b_1$ and $b_2$) or concentrations ($c_1$ and $c_2$). We assume that there is an imaginary sample from which the hybrid spectrum can be directly derived. The thickness of the imaginary sample, $b_x$, is given by

$$\phi_h = \phi_0 e^{-Kb_x} = \alpha\phi_0 e^{-Kb_1} + (1-\alpha)\phi_0 e^{-Kb_2} \tag{5}$$

It is well known from many textbooks on instrumental analysis that the optimum absorbance of a solvent should be about 0.4 [21]. On the other hand, anomalous absorption errors also limit a background sample to have strong bands [22]. Thus, we set the maximum absorbance of $b_2$ sample ($A_{max}$) being about 0.6, corresponding to $K_{max}b_2 = 1.4$.

Table 1 shows the relationship among $b_x$, absorption coefficient $K$, $b_2$ and $b_1$. Clearly, $b_x$ varies with the absorption coefficient. For example, $b_{x(100,\ 80)}$ is equal to 89.30 μm at $K=0.014$ while it becomes 90.00 μm at $K=0$. It should be mentioned here that the thickness of any real sample remains always constant regardless of the absorption coefficient. Therefore, as compared to a single-beam spectrum of a real sample, the hybrid spectrum should be distorted to a greater or lesser extent. Fig. 1a and b shows the IR spectrum of a 38 μm-thick polystyrene (PS) film and an IR hybrid spectrum of an imaginary PS film ($b_2$=38μm, $b_1$=0, α=0.5). The shapes and relative intensities of spectral bands in Fig. 1b are quite different from those in Fig. 1a, demonstrating that the improper choosing of $b_1$ and $b_2$ samples can lead to a seriously distorted hybrid spectrum. Fortunately, the distortion of the hybrid spectrum can be minimized if the ratio of $b_1/b_2$ is set to be close enough to unity, as discussed below.

The distortion of the hybrid spectrum can be accounted for correctly. As can be found from Fig. 1a: at 2923.7 cm$^{-1}$, absorbance=2.40054, $b$=38 μm, and then obtained $K$=0.14546; at 1801.3 cm$^{-1}$, absorbance=0.17895, $b$=38 μm, and obtained $K$=0.010843. It may be noted that $b_1$ is zero and α is 0.5 in the case of Fig. 1b, so that Eq. (5) may be rewritten as

$$\phi_h = \phi_0 e^{-Kb_x} = 0.5\phi_0 + 0.5\phi_0 e^{-38K} (b_2 = 38\ \mu m) \tag{5'}$$

**Table 1**
The relationship among the thickness $b_{x(b_2,b_1)}$ of the imaginary sample, absorption coefficient $K$ and the values of $b_2$ and $b_1$.[a,b]

| $b_x$ | $K$ | | | | |
|---|---|---|---|---|---|
| | 0.014 | 0.010 | 0.007 | 0.004 | 0.0 |
| $b_{x(100,80)}$ | 89.30 | 89.50 | 89.65 | 89.80 | 90.00 |
| $b_{x(100,70)}$ | 83.44 | 83.88 | 84.21 | 84.55 | 85.00 |
| $b_{x(100,20)}$ | 49.34 | 52.20 | 54.47 | 56.81 | 60.00 |

[a] $b_{x(100,80)}$, $b_{x(100,70)}$ and $b_{x(100,20)}$ , the thicknesses of the imaginary samples derived from (100 μm, 80 μm), (100 μm, 70 μm) and (100 μm, 20 μm) sample pairs under a component factor (α) of 0.5, respectively.

[b] The largest absorbance of $b_2$ sample (100 μm-thick) is equal to 0.60 ($Kb_2$=1.4).

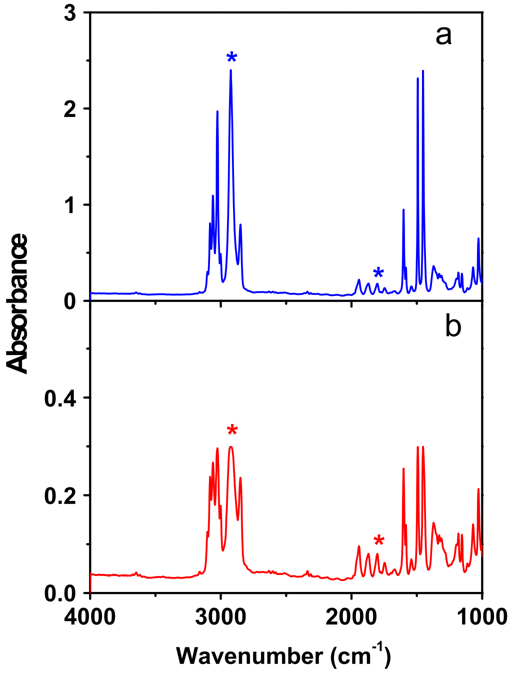

**Fig. 1.** (a) IR spectrum of a 38 μm-thick polystyrene (PS) film, and (b) IR hybrid spectrum of an imaginary PS film (16 scans of the PS film +16 scans of air, α=0.5). The background spectrum was measured by co-adding 32 times of air background.

**Table 2**
The spectral similarity comparison between the hybrid spectrum and its corresponding reference real spectrum.[a,b]

| $e^{-Kb}$ | $K$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0.014 | 0.011 | 0.0090 | 0.0070 | 0.0050 | 0.003 | 0 |
| $e^{-Kb_{x(100,80)}}$ | 0.2864 | 0.3738 | 0.4467 | 0.5339 | 0.6384 | 0.7637 | 1 |
| $e^{-89.65K}$ | 0.2851 | 0.3730 | 0.4463 | 0.5339 | 0.6387 | 0.7642 | 1 |
| $e^{-Kb_{x(100,70)}}$ | 0.31095 | 0.3979 | 0.4696 | 0.5546 | 0.6556 | 0.7757 | 1 |
| $e^{-84.21K}$ | 0.3076 | 0.3960 | 0.4687 | 0.5546 | 0.6564 | 0.7768 | 1 |
| $e^{-Kb_{x(100,20)}}$ | 0.5012 | 0.5677 | 0.6209 | 0.6830 | 0.7557 | 0.8413 | 1 |
| $e^{-54.47K}$ | 0.4665 | 0.5493 | 0.6125 | 0.6830 | 0.7616 | 0.8492 | 1 |

[a] $e^{-Kb_{x(100,80)}}$, $e^{-Kb_{x(100,70)}}$ and $e^{-Kb_{x(100,20)}}$ are the intensities of the hybrid spectra from (100 μm, 80 μm), (100 μm, 70 μm) and (100 μm, 20 μm) sample pairs under a component factor(α) of 0.5, respectively.

[b] $e^{-89.65K}$, $e^{-84.21K}$ and $e^{-54.47K}$ are the intensities of the spectra from 89.65, 84.21 and 54.47 μm-thick real samples, respectively.

Theory computation for the intensity of the hybrid spectrum: at 2923.7 cm$^{-1}$, $K=0.14546$, $\phi_0 e^{-Kb_x}=0.5\phi_0+0.5\phi_0 e^{-38K}=0.50199\phi_0$, then obtained $A=\lg\frac{\phi_0}{\phi_0 e^{-Kb_x}}=0.2993$; at 1801.3 cm$^{-1}$, $K=0.010843$, $\phi_0 e^{-Kb_x}=0.5\phi_0+0.5\phi_0 e^{-38K}=$ $0.83115\phi_0$, then $A=0.0803$. Found in Fig. 1b: at 2923.7 cm$^{-1}$, $A=0.2992$; at 1801.3 cm$^{-1}$, $A=0.0802$. The experimental data in Fig. 1b are excellently consistent with the computation results, strongly demonstrating the correctness of Eq. (5).

Why is the hybrid spectrum in Fig. 1b distorted significantly? The reason is that the imaginary sample has quite different thicknesses at different absorption coefficients, for example, 17.06 μm at 1801.3 cm$^{-1}$ ($K=0.010843$) and 4.74 μm at 2923.7 cm$^{-1}$ ($K=0.14546$).

In the following sections, the way how to obtain a hybrid spectrum with minimal distortion is discussed. The hybrid spectrum usually has many absorption bands. We should keep all the absorption bands free from significant distortion when using the hybrid spectrum as a single-beam background spectrum. In other words, the difference between the hybrid spectrum and its corresponding real spectrum at any wavenumber or $K$ value should be very small. To compare spectral similarity between a hybrid spectrum and its corresponding real spectrum, one band should be chosen as a matching reference. In the present study, the peak absorbance of a medium band ($K=0.5K_{max}$) in the corresponding single-beam spectrum of a real sample is chosen to match the intensity of the same band in the hybrid spectrum.

Table 2 lists the comparisons of the spectral similarity between a hybrid spectrum and its corresponding reference real spectrum, these two spectra have the same absorption intensity at $K=0.0070=0.5K_{max}$. As can be seen from Table 2, the spectral similarity is closely related to the values of $b_1$ and $b_2$. The greater the ratio of $b_1/b_2$, the more similar a hybrid spectrum to its corresponding real spectrum, i.e., the smaller the distortion of the hybrid spectrum. In theory, a hybrid spectrum can be obtained without any distortion when the ratio of $b_1/b_2$ is exactly equal to unity.

The spectral similarity is also strongly influenced by $K_{max}b_1$ and $K_{max}b_2$. If the ratio of $b_1/b_2$ and the component factor (α) are fixed, the smaller the largest absorbance ($A_{max}=\lg\frac{1}{T}=-\lg e^{-K_{max}b_2}=0.434K_{\max}b_2$), the smaller the distortion of the hybrid spectrum. The hybrid spectrum will be theoretically free from any distortion when $K_{max}b_2$ is arbitrarily close to zero.

The difference between a hybrid spectrum and its corresponding real spectrum at any $K$ value can be estimated quantitatively by the relative deviation (RD):

$$\mathrm{RD}=\frac{\phi_{real}-\phi_h}{\phi_{real}}\times 100\%=\frac{e^{-Kb}-e^{-Kb_x}}{e^{-Kb}}\times 100\%$$

Data in Table 2 shows that the maximum relative deviations (RDs) appear at $K=0.014$. The maximum RDs for $e^{-Kb_x(100,80)}$, $e^{-Kb_x(100,70)}$,and $e^{-Kb_x(100,20)}$are 0.46%, 1.0% and 7.4%, respectively. If the maximum RD between a hybrid spectrum and its corresponding real spectrum is less than 1%, the distortion would be small enough to consider the hybrid spectrum and its corresponding real spectrum being identical. Fig. 2 shows excellent spectral match between the hybrid spectrum ($\phi_0 e^{-Kb_x(100,70)}=0.5\phi_0 e^{-100K}+0.5\phi_0 e^{-70K}$) and its corresponding real spectrum ($\phi_0 e^{-84.21K}$). Thus, the hybrid spectrum of $\phi_0 e^{-Kb_x(100,70)}(\alpha=0.5)$ can be used to represent the real sample at a pathlength of 84.21 μm.

A medium band of the real sample is used as a matching reference, as discussed above. If the matching band is stronger than a medium band, the hybrid spectrum will be more similar to its new corresponding real spectrum. For example, the hybrid spectrum of $\phi_0 e^{-Kb_x(100,70)}(\alpha=0.5)$ and its new corresponding real spectrum of $\phi_0 e^{-83.44K}$ have the same absorption intensity at $K=0.014=K_{max}$. The maximum RD between them is about 0.54%, being much less than 1.0% (where a medium band is selected as a matching reference).

In summary, in order to keep the synthesized hybrid spectrum free from significant distortion, $b_2$ and $b_1$ samples should fulfill two conditions:

$$b_2>b_1\geq 0.7b_2 \quad \text{and} \quad A_{max}\leq 0.60$$

The spectral similarity is also influenced by the component factor (α). The closer the component factor to 0.5, the greater the distortion of the hybrid spectrum. The hybrid spectrum is the real spectrum of $\phi_0 e^{-Kb_2}$ at α=0 or the real spectrum of $\phi_0 e^{-Kb_1}$ at α=1. It should be noticed that all data in Tables 1 and 2 were obtained at α=0.5, the worst case. Therefore, under conditions of $b_2>b_1\geq 0.7b_2$ and $A_{max}\leq 0.60$, all the synthesized hybrid spectra are free from significant distortion regardless of the component factor. Consequently, $\phi_0 e^{-Kb_x(100,70)}$ $(\alpha\phi_0 e_{-100K}+(1-\alpha)\phi_0 e^{-70K})$

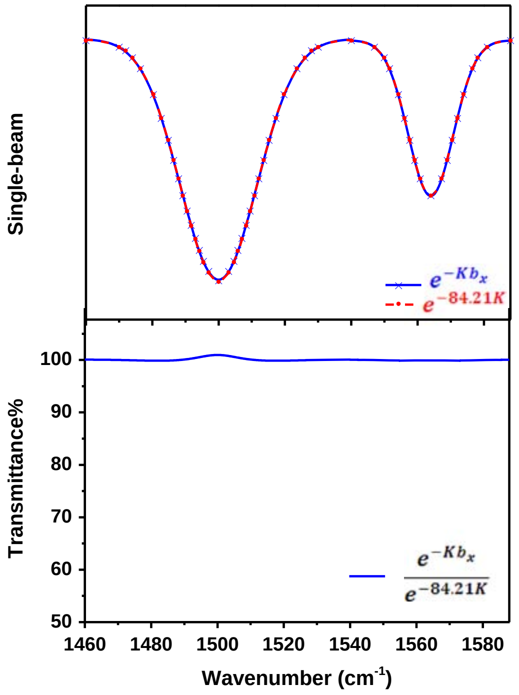

**Fig. 2.** Comparison between the simulated hybrid spectrum (– × –) and its corresponding real spectrum (– ● –).The hybrid spectrum is derived from (100 μm, 70 μm, $K_{max}=0.014$) sample pair under α=0.5, and the corresponding real spectrum has a thickness of 84.21 μm.

can represent the sample at any desired pathlength ranging from 70 to 100 μm by changing the value of α.

It is to be emphasized that if more excellent spectral match is required, either of two conditions described above can be changed according to experimental requirements of an analyst. Large ratio of $b_1/b_2$ and/or small $A_{max}$ ($K_{max}b_2$) would be beneficial in synthesizing a less distorted hybrid spectrum.

Similarly, for solution samples, the dilute ($c_1$) and the concentrated ($c_2$) solutions should meet the following conditions:

$$c_2 > c_1 \geq 0.7c_2 \quad \text{and} \quad A_{max} \leq 0.60$$

A unique advantage of the hybrid spectrum is that its intensity is closely related to the component factor. Thus, a hybrid background spectrum with any desired intensity within the range of $\phi_0 e^{-Kb_1}$ to $\phi_0 e^{-Kb_2}$ can be easily obtained simply by choosing an appropriate component factor (or an appropriate number of scans, in the case of Eq. (2)). This novel property may provide us a convenient way to obtain a quality absorbance/transmittance spectrum without background interference.

## 3. Experimental

$CH_2Cl_2$, $CCl_4$ (purity ≥ 99%) and 2-hexanone (Wako Pure Chemical Industries, Ltd., Osaka, Japan) are used without further purification. IR spectra of 2-hexanone were measured using a gas cell with 10 cm pathlength. $CH_2Cl_2/CCl_4$ solutions were prepared by adding 7.0, 8.0, and 9.0 ml of $CH_2Cl_2$ into 10 ml volumetric flask and then filling to 10 ml with pure $CCl_4$. The solutions were denoted as 70, 80 and 90% solutions, respectively. IR spectra of the solutions of $CH_2Cl_2/CCl_4$ were recorded by using a $BaF_2$ cell with 50 μm pathlength.

FT-IR spectra were obtained at a 4 $cm^{-1}$ resolution with a Nicolet 6700 FTIR spectrometer with a DTGS detector. Omnic software (Nicolet) provided a pause function during the scanning procedure. After taking $N_1$ scans through sample $b_1$, one may use the pause time to replace sample $b_1$ with sample $b_2$, and then continue to acquire the spectrum of sample $b_2$. Thus, a series of hybrid spectra can be obtained as the scanning proceeds.

## 4. Results and discussion

### 4.1. Atmospheric water vapor interference

For IR operators, water vapor is one of the most annoying components of the atmosphere. An IR spectrometer is usually hermetically sealed and desiccated, so that the only humid air is in the sample compartment of the instrument. Because the sample compartment often has to be open to room air for background and sample exchanges, the humidity of the air in the sample compartment normally fluctuates in the ensuing measurement time. Usually, the largest absorbance of water vapor is much less than 0.6 and the humidity fluctuation in the whole spectrometer is not large (but the humidity in the sample compartment may change rather greatly) during the measurement time for the single-beam sample or background spectrum. Thus, the use of an IR hybrid spectrum to eliminate water vapor interference is a good example. The hybrid single-beam spectrum of water vapor can be described by the following equation:

$$\phi_h = \alpha_1\phi_0 e^{-abc_1} + \alpha_2\phi_0 e^{-abc_2} + \cdots + \alpha_i\phi_0 e^{-abc_i} \qquad (6)$$

where $c_i$ is the concentration of water vapor during different number of scans, and $\alpha_1 + \alpha_2 + \cdots + \alpha_i = 1$.

A modern FTIR spectrometer can display the spectrum at every scan during the measurement. The acquisition of a quality IR spectrum without water vapor interference can be achieved simply by terminating the spectral measurement at the right moment by visual observation of the live display at each scan.

Fig. 3 shows IR spectra of 2-hexanone measured by the hybrid spectrum method with fluctuating humidity. A background spectrum was taken first. After initial 128 scans of the single-beam sample (2-hexanone) spectrum, water vapor peaks appear upwards (Fig. 3a), showing that the current sample spectrum contains more water vapor than the background spectrum measured in advance. Thus we then supplied dry air (or dry nitrogen) to the sample compartment of the instrument while continuing the scan. The peaks from water vapor gradually became smaller and smaller upon the continued scans (Fig. 3b), and eventually, the peaks of water vapor were reduced to almost zero at certain scan point (Fig. 3c). At this point, the spectral acquisition was terminated, and, a quality infrared spectrum with minimal water vapor interferences was obtained.

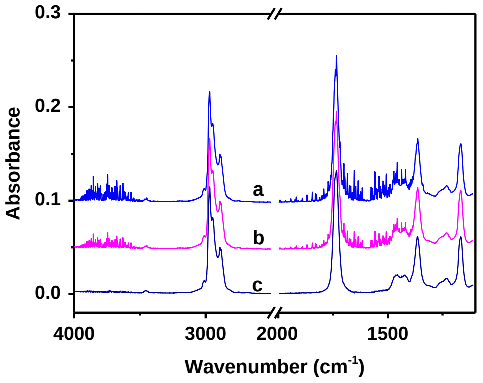

**Fig. 3.** IR spectra of 2-hexanone collected by the hybrid spectrum method at a resolution of 2 $cm^{-1}$, (a) $N_1=128$ scans, $N_2=0$ scans, (b) $N_1+N_2=192$ scans, and (c) $N_1+N_2=360$ scans. Dry air pulse was introduced to the sample compartment of the instrument after initial 128 scans ($N_1=128$).

### 4.2. IR spectra of $CH_2Cl_2/CCl_4$ solution

Fig. 4 shows how to remove $CH_2Cl_2$ bands from the solution of $CH_2Cl_2/CCl_4$. A $BaF_2$ cell with 50 μm pathlength was used for all the background and sample spectra. The single-beam sample spectrum was first collected by co-addition of 64 scans through 80% $CH_2Cl_2/CCl_4$ solution. Then, the hybrid single-beam background spectrum was acquired by scanning 70% solution for 128 times ($N_1$), followed by scanning 90% solution for $N_2$ times. Both the dilute (70%) and the concentrated (90%) solutions meet the conditions of $A_{max} \leq 0.60$ and $c_1 \geq 0.7c_2$.

From Fig. 4a ($\alpha=1$, $N_2=0$), to b ($\alpha=0.73$, $N_2=48$), c ($\alpha=0.58$, $N_2=92$) and to d ($\alpha=0.48$, $N_2=136$), the intensities of $CH_2Cl_2$ bands at 3055 and 2989 $cm^{-1}$ decrease gradually. At the point of $N_2=136$, the intensities of $CH_2Cl_2$ bands became unobservable, thus the desired single-beam spectrum or the desired quality transmittance spectrum was attained (Fig. 4d). Fig. 4 strongly demonstrates that the proposed method can be applied to both relatively weak bands and more intense bands.

It should be recognized that the component factor in Eq. (2) cannot take any arbitrary value because of the nature of integer numbers. The greater the number of $N_1$, the smaller the intervals of the two neighboring α values. Thus, large $N_1$ will make the variation of α more smoothly. In the near future, the algorithm will be developed by Eq. (3), where alpha can take an arbitrary value between zero and unity.

### 4.3. Comparison with spectral subtraction

Spectral subtraction is a powerful and widely used method to eliminate background interference. In the following, the hybrid spectrum method was compared with the spectral subtraction method.

As shown in Fig. 3c, our hybrid spectrum method can exactly match the level of water vapor in the sample and background spectra, while the experiments by Weis [22] and Ulman [9] showed that it was difficult to remove water vapor interference completely by the spectral subtraction technique. Comparison of Fig. 5a and b shows that the hybrid method works better and more effectively. Moreover, excellent 100% line can be collected by hybrid spectrum method, see the supplementary material, while the spectral subtraction technique would give both positive and negative residual absorption peaks [22]. Therefore, the hybrid spectrum method is a highly effective technique for eliminating the background interference.

The measured spectrum should always be converted to absorbance before any spectral subtraction operation. Conversely, the hybrid spectrum method can be directly applied to measurements of spectra with any ordinate scale including transmittance, reflectance, absorbance, etc., because the hybrid spectrum is a single-beam spectrum indeed. To the best of our knowledge, this may be the first time that a single-beam spectrum with the desired intensity has ever been easily achieved.

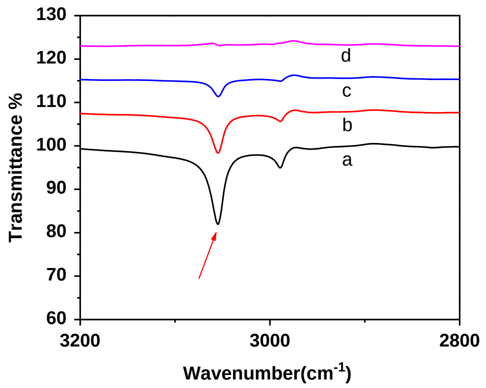

**Fig. 4.** IR spectra of $CH_2Cl_2/CCl_4$ solution. The hybrid single-beam background spectrum was obtained by 128 ($N_1$) scans of 70% solution $+N_2$ scans of 90% solution: (a) $N_2=0$, (b) $N_2=48$, (c) $N_2=92$, and (d) $N_2=136$.

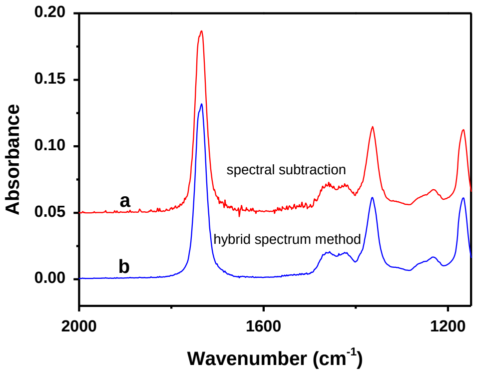

**Fig. 5.** Comparison of IR spectra of 2-hexanone obtained by (a) spectral subtraction and (b) hybrid spectrum method.

The hybrid spectrum contains spectral information from both $c_1$ and $c_2$ solutions while the subtrahend spectrum in spectral subtraction arises merely from $c_1$ (or $c_2$) solution. In general, the combination of $c_1$ and $c_2$ solutions describes the sample signal in $c$ solution ($c_1 < c < c_2$) more accurately than $c_1$ solution alone. For example, it is not always possible to perform a good spectral subtraction, as the minuend spectrum may be unavoidably nonlinear. However, if the difference between $c_2$ and $c_1$ is small enough, the signal of c solution may be correctly represented by a hybrid spectrum whether Beer's law is obeyed or not (the squeeze theorem in spectroscopy).

The main drawback of the hybrid spectrum method is the spectral distortion. However, under optimized conditions, the spectral distortion can be strictly controlled to very small deviation, as shown in Fig. 2. The use of a hybrid spectrum has another weak point. A relatively strong (a medium band or stronger band) and independent band from the hybrid spectrum is required as an internal intensity standard. If all strong bands of the hybrid background spectrum overlap with the sample bands of interest, problems may occur due to the lack of the indicator.

## 5. Conclusions

In the present study, we have proposed the infrared hybrid single-beam spectrum method. The water vapor bands and $CH_2Cl_2$ bands were successfully and completely removed by adopting the hybrid spectrum method. The main conclusions of the present study are:

(1) If two appropriate IR samples are chosen, namely under conditions of $b_2 > b_1 \geq 0.7b_2$ and $A_{max} \leq 0.60$, all the synthesized hybrid single-beam spectra will be free from significant distortion regardless of the component factor.
(2) The intensity of the hybrid spectrum can be continuously adjusted by the component factor (or number of scans). Thus, a hybrid spectrum with the desired intensity can be easily obtained.
(3) The high effectiveness of hybrid spectrum method (spectral division) is evident in its capability to eliminate the background interference completely.
(4) Because of the nature of the single-beam spectrum, the proposed hybrid spectrum method can be applied to remove

background interference whether the ordinate is absorbance or not.

## Acknowledgment

This project was supported by Grant 20873136 from the Natural Science Foundation of China

## Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.10.058.

## References

[1] J.M. Chalmers, P.R. Griffiths, Handbook of Vibrational Spectroscopy, John Wiley & Sons Ltd., Chichester, 2002.
[2] P.R. Griffiths, J.A. de Haseth, Fourier Transform Infrared Spectroscopy, 2nd ed., John Wiley & Sons Ltd., Hoboken, New Jersey, 2007.
[3] A.A. Christy, Y. Ozaki, V.G. Gregoriou, Modern Infrared Spectroscopy: Principles and Applications, Amsterdam, Elsevier Sciences, 2001.
[4] M. Diem, M. Romeo, S. Boydston-White, M. Miljkovic, C. Matthaus, Analyst 129 (2004) 880–885.
[5] M. Banno, K. Iwata, H. Hamaguchi, J. Chem. Phys. 126 (2007) 204501.
[6] Z.W. Yu, L. Chen, S.Q. Sun, I. Noda, J. Phys. Chem. A 106 (2002) 6683–6687.
[7] Y.Q. Wu, K. Murayama, Y. Ozaki, J. Phys. Chem. B 105 (2001) 6251–6259.
[8] V.P. Tolstoy, I. Chernyshova, V.A. Skryshevsky, Handbook of Infrared Spectroscopy of Ultrathin Films, John Wiley & Sons, New York, 2003.
[9] A. Ulman, An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly, Academic Press, San Diego, California, 1991.
[10] M. Boulet, T. Lefevre, T. Buffeteau, M. Pezolet, Appl. Spectrosc. 62 (2008) 956–962.
[11] L. Shao, P.R. Griffiths, A.B. Leytem, Anal. Chem. 82 (2010) 8027–8033.
[12] H.A. Willis, J.H. van der Maas, R.G.J. Miller, Laboratory Methods in Vibrational Spectroscopy, 3rd ed., John Wiley & Sons, New York, 1987.
[13] L.M. Ng, R. Simmons, Anal. Chem. 71 (1999) 343R–350R.
[14] Y.Z. Jia, S.Y. Gao, S.P. Xia, J. Li, Spectrochim. Acta A, Mol. Biomol. Spectrosc. 56 (2000) 1291–1297.
[15] P. Saini, J.C. Lai, D.R. Lu, J. Pharm. Biomed. Anal. 12 (1994) 1091–1095.
[16] J.R. Powell, F.M. Wasacz, R.J. Jakobsen, Appl. Spectrosc. 40 (1986) 339–344.
[17] D.C. Lee, P.I. Haris, R.C. Mitchell, Biochemistry 29 (1990) 9185–9193.
[18] K.A. Oberg, A.L. Fink, Anal. Biochem. 256 (1998) 92–106.
[19] K. Rahmelow, W. Hubner, Appl. Spectrosc. 51 (1997) 160–170.
[20] M. van de Weert, P.I. Haris, W.E. Hennink, D.J.A. Crommelin, Anal. Biochem. 297 (2001) 160–169.
[21] G.D. Christian, Analytical Chemistry, 5th ed., Wiley, New York, 1994.
[22] D.D Weis, G.E Ewing, Anal. Chem. 70 (1998) 3175–3183.