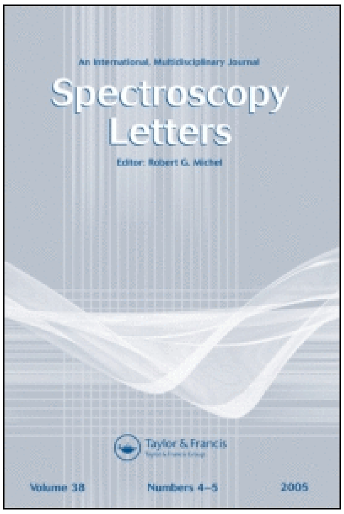

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REMOTE FOURIER TRANSFORM INFRARED EMISSION SPECTROSCOPY IN THE STUDIES OF THE SOLID PROPELLANT COMBUSTIONS①

Key Words: Remote Sensing; Gas Analysis; Spectral Radiance; Molecular Emission Spectra; Fourier Transform Infrared Spectroscopy

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Abstract

In this paper infrared emission spectra of the solid propellant combustion using remote Fourier transform spectroscopy have been studied. Both the infrared spectral radiance distributions and gas quantitative method for solid propellant combustions by remote Fourier transform infrared emission spectroscopy have been presented. In the method we utilize estimating tem-

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perature measuring models, which are modified by Junde Wang, based on emission fundamental band measurements of HCl or HF. Through measuring the temperature both the infrared spectral radiance distributions of the solid propellant combustions and their emisivities can be obtained. A remote measured gas concentration model based on combustion temperature, spectral radiance and emissivity has been developed. Field single-ended measurements at long distances for solid propellant plumes at temperature 1700-3500K can be extended to measuring fluctuations of instantaneous temperature and combustion reaction products.

I . INTRODUCTION

The measurement of gaseous species in a flame has already attracted more and more interests to scientists. The main reason is that it gives off harmful species, such as carbon dioxide (CO_2), fluorine hydride (HF), chlorine hydride (HCl), ammonia (NH_3), etc. , which not only pollute the environment, but also do harm to human health. Therefore, determining concentrations of these species have become very important in analytical chemistry.

The aim of the measuring infrared spectral radiance distribution of the solid propellant combustion not only is to determine gas concentration, but also is to provide theoretical and experimental bases for the design of some infrared guidance and anti-guidance systems.

The use of Fourier transform infrared (FTIR) spectroscopy which has been developed over the past decade is becoming increasingly popular and significant in analytical chemistry, due to its several advantages, such as multiplex (that is , FTIR spectrometer receives information about the entire spectral range during an entire scan. This is a statement of the Fellgett or multiplex advantage), and throughput (That is, the ability of FTIR spectrometer to collect a large amount of energy at high resolution was expressed by Jacquinot as a throughput advantage.). Herget[1-3] and Junde Wang[4,5] have applied remote FTIR spectroscopy to some pollution remote measurements. Carlson[6] observed effluents from small building smokestacks using FTIR spectroscopy. Stearns[7] reported airborne FTIR observations and analyses of a large forest fire. The advantages are (1)long-path (about a kilometer)absorption measurements in the atmosphere and (2) single-ended remote emission measurements beside these advantages mentioned above for FTIR. Specifically, such measurements would require no prior knowledge of anticipated, no sample handling. In this study, we have made full use of advantages of remete FTIR to make remote sigle-ended emission measurement for very weak emission from hot gas components in flame combustions. Very weak molecular bands of HF or HCl in infrared emission have been also observed. By establishing a theoretical and quantitative method, typical concentrations for CO_2, HCl, HF and NO in the combustion products of the solid propellant have been determined through emission bands measured using remote sensing FTIR system.

Ⅱ. THEORY

According to Beer's absorption law, the relation between gas concentration and the energy transmitted at a given wavenumber may be expressed as

$$\tau(\nu) = exp(-KC'L) \qquad (1)$$

where v is the wavenumber (cm^{-1}), $\tau(v)$ is the transmittance of infrared source energy, K is the spectral absorption coefficient ($atm^{-1}cm^{-1}$ or $ppm^{-1}m^{-1}$), C' is the concentration, L is the pathlength of the infrared source.

Once the temperature (T) of the infrared source is determined, its emissivity $\varepsilon(v)$ at the wavenumber v(cm^{-1}) can be given expticitly by

$$\varepsilon(\nu) = \frac{N(\nu)}{H(\nu, T)} = 1 - \tau(\nu) \qquad (2)$$

where N (v) is the spectral radiance (watts • cm^{-2} • $steradian^{-1}$ • $wavenumber^{-1}$)of the infrared source at the temperature(T), H(v, T) is the spectral radiance of a blackbody at the infrared source temperature (T), in other words, H(v,T) is the Planck's blackbody radiation function at temperature (T). The system software has the capability of generating the Planck's blackbody radiation function for any desired blackbody temperature. From Eqns(1) and (2) the concentration can be obtained

$$C' = -\frac{ln[1 - \varepsilon(\nu)]}{KL} \tag{3}$$

where C′ is the concentration uncorrected by the temperature.

In actual measurement, the effect of the source temperature (T) on the concentration of gaseous species needs to be considered. The calibration of the concentration may be given as

$$C = C'(\frac{T}{273}) \tag{4}$$

where C is the concentration considering temperature.

If gas emissivity $\varepsilon(v)$ and spectral absorption coefficient K of gaseous species are known, its concentration would be calculated from Eqns(3) and (4). In view of these considerations, several steps have been taken in this as follows

Remote FTIR spectrometer system calibration

To obtain spectral emissivity $\varepsilon(v)$, it is first necessary to make spectral radiance measurements. Spectral radiance measures the flux of radiation leaving the source per unit area. Emission spectra are calibrated in terms of spectral radiance by comparison with the spectrum of a blackbody radiation source at known temperature. This is measured properly only when the source or the blackbody calibration system totally fills the instrument field of view.

For a blackbody at known temperature T its single beam $S_b(v)$ measurement will yield[8]

$$S_b(\nu) = R(\nu)H(\nu,T) + B(\nu) \tag{5}$$

where T is known temperature (degrees Kelvin), v is frequency in wavenumber (cm^{-1}), H(v,T) is Planck′s function of absolute blackbody at given temperature, R(v) is the instrument response function of this system, B(v) is the background including the instrument background and environmental background around the infrared source. It is noteworthy that background radiation reflected by the gas is eliminated in Eqn(5).

From Eqn(5) we have

$$R(\nu) = \frac{S_b(\nu) - B(\nu)}{H(\nu,T)} \tag{6}$$

To do this, a blackbody operated at given temperature T is placed to fill the field of view of receiver telescope of remote FTIR spectrometer. The background interferogram is subtracted from the blackbody interferometer, then the result is transformed into single-beam spectrum S_b. Lastly, CO_2 and H_2O absorptions in the atmosphere are removed from the single-beam spectrum S_b and a standard blackbody single-beam spectrum W(v) is obtained; thus

$$W(\nu) = S_b(\nu) - B(\nu) \tag{7}$$

so

$$R(\nu) = W(\nu)/H(\nu,T) \tag{8}$$

For the spectral radiance N(v,T) of any desired source, we have

$$N(\nu,T) = \frac{S(\nu,T) - B(\nu)}{R(\nu)} \tag{9}$$

Where S(v,T) is the single-beam spectrum of the desired source, B(v) is the single-beam emission spectrum of the background.

From Eqns (2-4) and (9), we can obtain emissivity ε(v) and concentration of desired gas, respectively.

Ⅲ. EXPERMENTAL

1. Instrumentation

The infrared emission spectra were recorded on a Nicolet 170 Remote source FTIR spectrometer system. In the spectrometer operated as a single-ended system a telescope in 2 inch diameter size is used to collect IR emission signals from sources, such as flame, lecated far apart the spectrometer. A ZnSe beamsplitter which it not hydroscopic is employed in the system. This instrumental configuration was previously described in detail[4].

2. The infrared sources

Two kinds of the solid propellants as the infrared sources are used in the study. One is the solid propellant containing a large quantities of ammonium perchlorate $(NH_4)ClO_4$. Other contains a large quantities of Teflon. All of them contain magnesium powder. Their sampling amounts are 50g.

When the solid propellants are burned, fluorine hydride (HF), chlorine hydride (HCl) and carbon dioxide (CO_2) are produced.

The distance between the flare and spectrometer is about 20m. The diameters of the flares are about 0. 5m.

3. Measurement proceduce

(1)System calibration

A blackbody (Model 11-210, Barnes Engineering Comp. , U. S. A.) is used for the calibration of the remote Fourier transform infrared system to obtain instrument response function $R(v)$. It is necessary to point out that theoretical instrument response function is only related to wavenumber and irrelative to temperature of the blackbody used. But practically, instrument response function is often affected by blackbody temperature. We had found that the instrument response function is almost irrelative to blackbody temperature when it is over 623K. So we select the temperature of blackbody operated to be 1273 K to obtain the instrument response function of this system in the study.

(2)Infrared spectrum collection

The system receives an external beam from the remote flare of the solid propellant to be measured. The beam travels through a collecting telescope that focuses the beam on the instrument aperture. The beam is then collimated and directed into interferometer to obtain the single-beam emission spectrum $S(v,T)$ of the desired source. The single-beam emission spectrum $B(v)$ of the background is obtained when the infrared source is not in operation (or by aiming the optics away from the infrared source).

(3)The temperature calculation

We can obtain the temperature of the flare from the rotation-vibration emission fundamental band of the molecules for HCl or HF[9,10].

(4)Spectral radiance calculation

From emission spectrum $S(v,T)$ of the desired source and the background emission spectrum $B(v)$ measured, the spectral radiance $N(v,T)$ of infrared source can be obtained with Eqn(9) through the system software.

(5)The concentration calculation

From the spectral radiance $N(\nu,T)$, gas emissivity $\varepsilon(\nu)$ and concentration C of the desired gas can be obtained through Eqns(2), (4) and (5).

IV. RESULTS AND DISCUSSION

1. Infrared emission spectra

The infrared emission spectra obtained from burning the solid propellants containing ammonium perchlorate or teflon are shown in Figs. 1 and 2, respectively. The spectra, which are the results of 4 coadded scans, are their spectral radiance distributions in 4200-800 and 5200-800 cm^{-1} wavenumber regions (All resolutions are 4 cm^{-1}). The lower wavenumber limit (i. e. 800cm^{-1}) is due to the poor efficiencies of the ZnSe beamsplitter, ZnSe telescope and MCT detector.

From these figures we observe CO_2, H_2O, HCl and HF infrared emission bands, and also CO_2 and H_2O infrared absorption bands.

2. From infrared spectral theory we can know that in the absence of carbon dioxide absorption the CO_2 emission band has a band centre at 2294 cm^{-1}. Because a strong infrared absorption band of the carbon dioxide molecule occurrs at 2349 cm^{-1}(corresponding to $00^{\circ}0 \leftarrow 00^{\circ}1$), the atmospheric carbon dioxide absorption results in the CO_2 emission band (2294 cm^{-1}) splits into three peaks presented in Figs. 1 and 2. The three emission peaks of the asymmetric-stretching emission band for carbon dioxide molecule are at 2240, 2280 and 2390 cm^{-1}, respectively. The two peaks at 2280 and 2240 cm^{-1} appear at slightly smaller wavenumbers, and other at 2390 cm^{-1} appears at slightly bigger wavenumber than the CO_2 absorption band at 2349 cm^{-1}.

3. Water emission bands indicated in Fig. 1 from the combustion of solid propellant containing ammonium perchlorate [$(NH_4)ClO_4$] appear in the 3800-3200, 2200-1700, and 1350-1150 cm^{-1} spectral regions. However, these emission bands don't interfere in the detection of other gases.

4. The rotation fine structure of hydrogen chloride emission band in the 3150-2425 cm^{-1} spectral region shown in Fig. 1 can be clearly re-

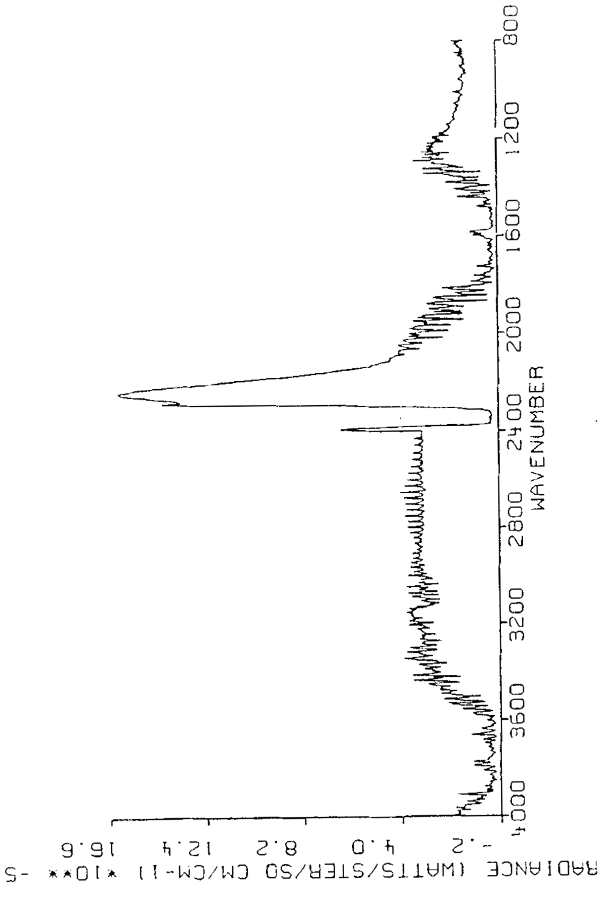

Fig. 1. Infrared emission spectrum of the solid propellant containing ammonium perchlorate.

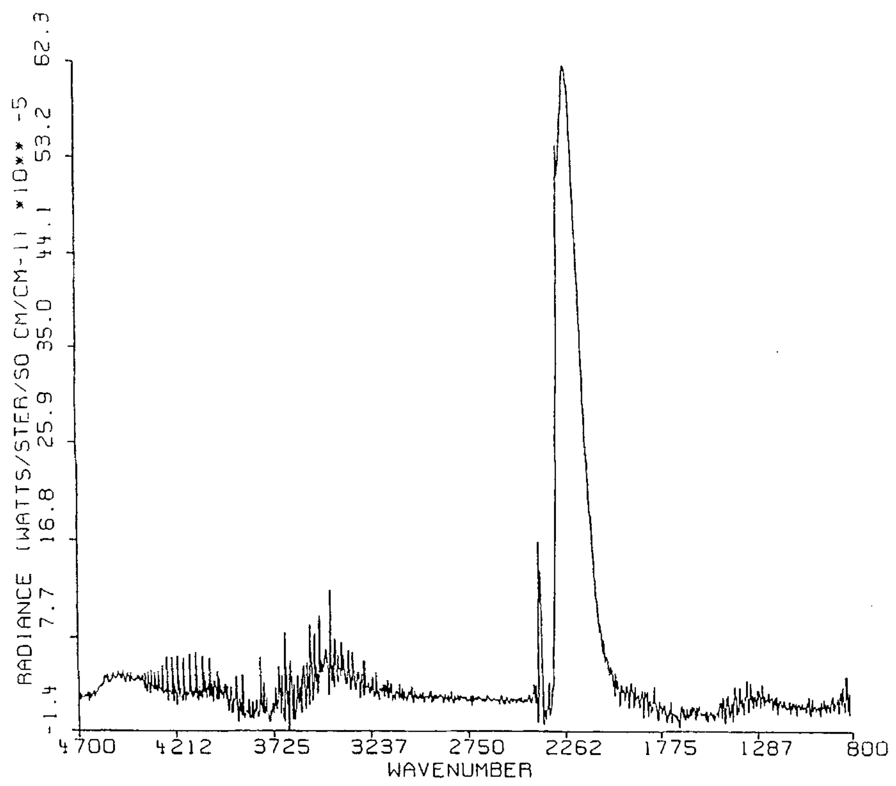

Fig. 2. Infrared emission spectrum of the solid propellant containing teflon.

solved. It is noted that the asymmetry of the intensities for the R (ν_R going from $\nu_0 = 2885$ cm^{-1} toward shorter wavelengths) and P (ν_p going toward longer wavelengths) branches, which correspond to the 3150-2906 and 2865-2425 cm^{-1} respectively, is due to the intensity of the R branch is interfered by H_2O emission band. ν_0 is only the gap[11].

5. The nitric oxide (NO) emission band occurs in the 1600 cm^{-1} shown in Fig. 2.

6. The spectrum shown in Fig. 2 is obtained when the solid propellant contained a large amount of teflon $\{[-CF_2-CF_2-]x\}$, about 34%, is

Table 1. Temperature and concentration determination of hot gas for burning solid propellants

Sample	L Diameter of flare(cm)	T (K)	Species	ν (cm^{-1})	K(ν)	ε	τ (1−ε)	C (ppm)
Solid propellant containing ammonium perchlorate	50	3362.7	CO_2	2245	0.34 $(cm \cdot atm)^{-1}$	8.2×10^{-5}	0.99992	57.9
			HCl	2820	10 $(cm \cdot atm)^{-1}$	4×10^{-6}	0.999996	0.12
			NO	1600	3 $(cm \cdot atm)^{-1}$	4×10^{-6}	0.999996	0.37
Solid propellant containing Teflon	50	1820.0	CO_2	2245	0.34 $(cm \cdot atm)^{-1}$	1.7×10^{-1}	0.83	7.3×10^{4}
			HF	4173	5.14×10^{-3} $(ppm \cdot m)^{-1}$	6.9×10^{-3}	0.993	18.2

burned. The HF emission band appears at the 4400-3200 cm^{-1} spectral region. The HF emission band at 4400-3960cm^{-1}shows significant rotation-vibration fine structure.

7. The temperatures of hot gases of burning solid propellants could be remotely estimated by the graphical method[9] of the individual line intensities in fine structure of the fundamental bands for HCl or HF, for example, the P branch of the principal emission band (fundamental) of HCl at 2890.1 cm^{-1} and the R branch of fundamental band of HF at 3966 cm^{-1}, or maximum intensity line in molecular emission fundamental band[10]. The temperatures for two kinds of the solid propellants are estimated as follows

$T_{(NH_3)ClO_4} = 3362.7$ K for the solid propellant containing ammonium perchlorate.

$T_{teflon} = 1820.0$ K for the solid propellant containing teflon.

8. According to Eqn(2) and infrared emission spectral radiance distributions shown in Figs. 1 and 2, the relation between the emissivity and the wavenumber for hot gas of burning solid propellants can be obtain.

9. Gas concentrations measured are listed in Table 1.

V . SUMMARY

1. Infrared emission spectral radiance distribution of combustion for solid propellants has been studied with remote FTIR spectroscopy.

2. Combustion temperatures of some solid propellants have been estimated directly remotely from rotational fine structure of molecular infrared spectra.

3. The concentration of some gaseous species with an infrared active vibrational transition, such as CO_2, HCl, HF and NO, have been measured remotely.

4. Several parameters on physical and chemical characteristics for hot gas can be measured simultaneously.

5. The method has the potential for analytical chemistry and combustion chemistry.

6. Measurements of this type are very importants for a number of applications for physics, chemistry and space technology.

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