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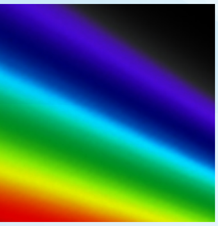
Combustion Analysis with HORIBA M-Series Spectrometers and Synapse CCD

OSD-AN-114

ELEMENTAL ANALYSIS
FLUORESCENCE
GRATINGS & OEM SPECTROMETERS
OPTICAL COMPONENTS
FORENSICS
PARTICLE CHARACTERIZATION
RAMAN
SPECTROSCOPIC ELLIPSOMETRY
SPR IMAGING



Tailoring fuel and explosives properties

Introduction

The chemistry of combustion is critical to a growing number of processes and industries-the petroleum and automobile industries are obvious examples. Airline, space, explosives and utilities industries are other examples. A detailed understanding of the processes involved in specific combustion applications allows the tailoring of the properties of the fuel or explosive to produce a more efficient, cleaner or powerful product. The internal energy state populations are representative of the local chemical combustion process. Because of the CCD's two-dimensional nature, it is possible to probe the combustion process at various points with USB interface, coupled to a Synapse Back-Illuminated UV CCD. The sample under investigation was the flame of a propane torch. The flame was imaged on to the entrance slit of the 1000M with a 50 mm focal length quartz lens mounted on an optical rail.

The 1000M spectrometer was equipped with a 1200 gr/mm grating blazed at 500 nm. A grating blazed at 330 nm would increase the signal significantly.

The second set of data was collected with a iHR550, 0.5-meter spectrometer, fitted with a room temperature PMT (1911F, R928). The input optics were the same.

Results and Discussion

One method used to study combustion is to monitor the hydroxyl radical (OH•) chemiluminescence. The emission spectrum of a flame or combustion process in the region around 310 nm is based on the transition from the $X^2\pi$ ground state to the $A^2+\Sigma$ excited state. The rotational temperature and vibrational population distribution of the A2+∑ state can be determined from the data. The hydroxyl radical can also be used to monitor different regions of the flame because it has a short lifetime, 0.66 µs. At 3000 K the population of the A2+∑ state is about 10^{-7} of the ground state from thermal effects. The excited state population is caused by direct exothermic chemical reaction.

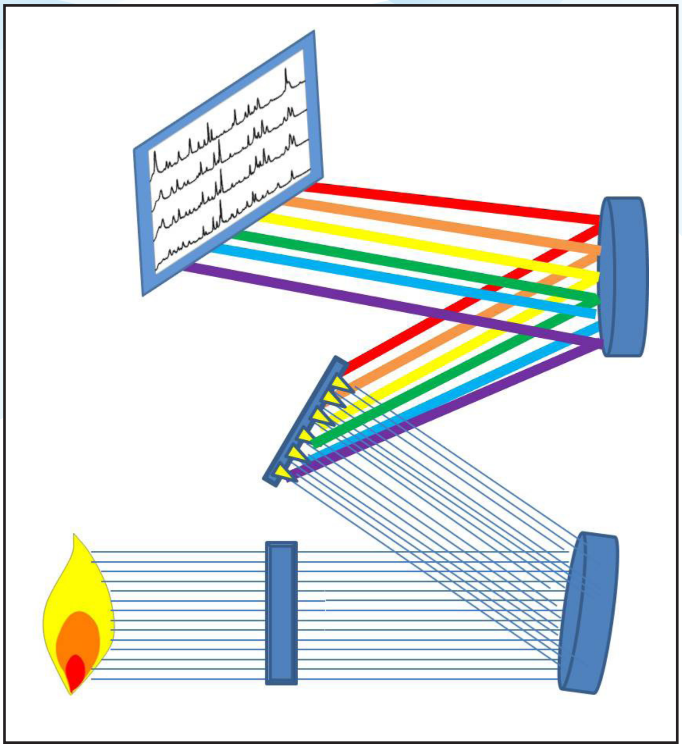


Figure 1. Diagram of imaging of flame onto the CCD

The OH emission occurs between 306 and 316 nm and contains most of the 0-0 vibrational band of the A2+∑ - X^2 electronic transition of OH as well as most of the 1-1 transition. The 0-0 bands fall below 312.1 nm and the 1-1 bands lie above this value. This fact can be used to determine the relative population of the v' = 0 and v' = 1 vibrational states. This requires calculation of theoretical spectra, which is beyond the scope of this application. For those readers who are interested, we suggest reading references 1 and 2. The vibrational population of OH can provide insights into the chemistry taking place in the combustion.

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The strongest peak at 309 nm is the Q2 (0-0) band head, and is primarily dependent on the population of lowest four rotational levels of the v' = 0 state. The other peaks have significant contributions from higher rotational levels and will vary in intensity relative to the Q2 head as a function of temperature. The relative intensities of the two peaks between 306 and 308 nm to the 309 nm peak can determine the rotational temperature of the flame.

Figure 2 shows an OH emission spectrum from the hot area of the flame. It was obtained with 0.06 nm resolution and a 0.2 second integration time. Note the fine structure evident in many of the peaks. The high resolution of the 1000M makes it possible to see this structure, even with a multichannel detector. The combination of the 1000M with the Synapse CCD delivers the resolution necessary to see the fine details and the speed to capture the data quickly. This can be particularly important when monitoring explosives and other transient processes. Resolving the structure of the spectrum is important to obtain information about the chemistry taking place. Speed of data acquisition is necessary to monitor relative changes in peak intensities. The Synapse CCD can acquire data on a millisecond scale.

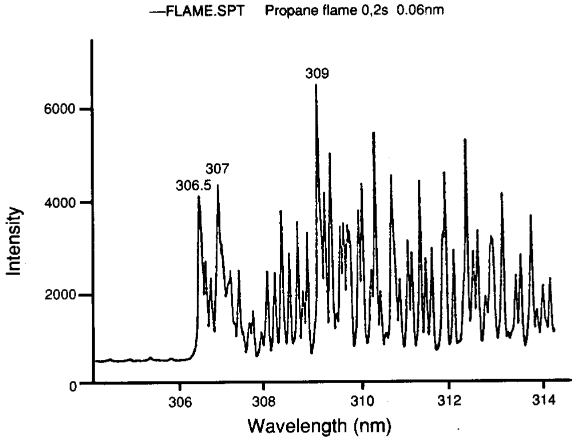

Figure 2. Chemiluminescence spectrum of OH radical produced in propane flame. The spectrum was obtained with a HORIBA 1000M, 1.0-meter spectrometer, fitted with a Synapse CCD. The resolution is 0.06 nm, the exposure time was 0.2 seconds.

The two-dimensional character of the CCD also allows you to monitor the OH chemi-luminescence as a function of position in the flame. This provides information about the temperature and chemistry at different positions within the flame. It is important to do this simultaneously to eliminate any variations due to fluctuations. To do this experiment, the flame was moved further away from the spectrometer and oriented parallel to the entrance slit in order to image the entire flame on the entrance slit. We then acquired 25 spectra simultaneously by splitting the CCD into 25 equal regions. Figure 3 is a three-dimensional plot of the data showing every fifth spectrum and only the 0-0 bands for clarity.

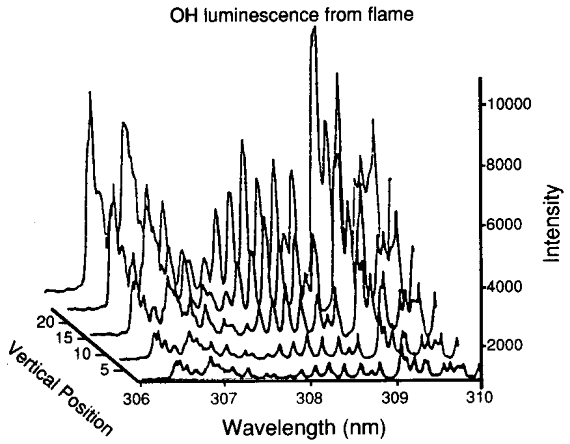

Figure 3. A 3-D plot of selected spectra from the 25 spectra obtained simultaneously by splitting the CCD into 25 regions. For clarity, only every fifth spectrum was displayed. This shows variations in the flame along the height of the flame.

This data permits us to estimate the rotational temperature of the A2+∑ state at various points along the length of the flame. To illustrate this, we selected three spectra, the first, twelfth and twenty-fifth, which represent the bottom, middle, and top of the flame. The spectra were first normalized to the 309 nm peak after subtracting a constant background. The ratio of the intensity of the 306.5 and 307 nm peaks to the intensity of the 309 nm peak was calculated. These results are given in Table 1. The ratios were compared to results given in reference 2 to obtain an estimate of the rotational temperature (TR) as a function of position. The results indicate a decrease in TR of about 400 K from the bottom of the flame to the top of the flame. This is summarized in Table 1.

For applications which do not require the ultimate in resolution, speed or positional information, an iHR550 and PMT are an economical alternative. Figure 4 shows the spectrum of the propane flame obtained with the above system. The resolution (0.14 nm) was set to provide reasonable data collection time (12 min), while still observing most of the details. The resolution could be improved at the expense of throughput and time required to collect the data. Because a large area PMT with full slit height was used to obtain this data, any calculated temperature or population will be average values. While this is adequate for many applications, it lacks the positional information and the speed of a CCD.

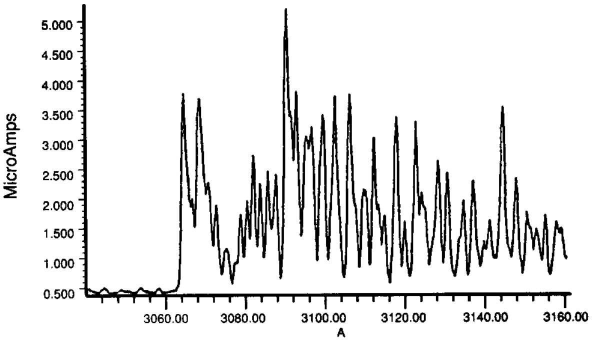

Figure 4. A spectrum of the propane flame obtained with a HORIBA iHR550, 0.5- meter spectrometer, and a PMT. The resolution was 0.1 nm and the integration time was 0.5 seconds.

Conclusion

The larger HORIBA spectrometers such as the 1.0-meter 1000M or 1.25-meter 1250M provide the resolution (0.06 nm in this case) necessary to resolve the fine structure found in many of the spectra from combustion processes. They also deliver excellent throughput so that when coupled to a HORIBA Synapse CCD the data can be acquired quickly. The two-dimensional nature of the CCD provides the ability to monitor different portions of the flame or combustion processes simultaneously.

These capabilities can lead to a greater understanding of the particular combustion process so that scientists can design cleaner more efficient fuels or engines or more powerful propellants or explosives.

This application note outlines how the complete system of 1000M-SII spectrometer with Synapse CCD can provide easy-to-use package to acquire and analyze the data. Once a model for a particular combustion process has been developed, the whole procedure of data collection and comparison to the model can be automated with a keystroke program. For example, the program could acquire the data, subtract a background, normalize the spectra, calculate the intensity ratios or several peaks and compare them to the model.
The iHR550 + PMT produce an economical system which delivers the necessary performance when instantaneous and positional information is not required. Positional data could be obtained by limiting the slit height and moving the sample vertically along the slit. This will significantly increase the data acquisition time. Also because the data would be collected at different times, any temporal relationship between the positional data will be lost.

References

1. J.A. Vanderhoff, A. J. Kottar, and M. W. Teague, "Temperature and Concentrations of Combustion Radicals Obtained by Computer Fitting Absorption Spectra", 27th JANNAF Combustion Subcommittee Meeting, Vol. 1, pp 543-549 (1990).

2. D.H. Campbell and S. Hulsizer, "Solid Propellant Combustion Zone Structure from Analysis of Hydroxyl Radical Chemi-luminescence," J. Propulsion, Vol. 2, pp 414-422 (1986).

	I_{309}	I_{307}	$I_{306.5}$	$I_{309/307}$	$I_{309/306.5}$	T_r
Propane 1	3713	2339	2451	0.63	0.66	2000
Propane 2	3942	2759	2523	0.70	0.64	2000
Propane 3	849	459	484	0.54	0.57	1600

Table 1. Rotational temperature of OH radical at the bottom, middle and top of the flame. I_x is the intensity of the peak at the indicated wavelength in nm, TR is the rotational temperature calculated from the ratios of the intensity at 307.0 and 306.5 nm to the intensity at 309.0 nm.

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