Spectral Study of Metallic Molecular Bands in Hybrid Rocket Plumes

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ABSTRACT

A labscale hybrid rocket was used to study spectral bands produced by metal combustion. Bands in the ultraviolet-visible region (300-750 nm) are of interest. The rubber-like fuel, hydroxyl-terminated polybutadiene (HTPB), was doped with a metallic salt for introduction into the plume during combustion. When introduced, the metals produce atomic line emissions as well as molecular bands due to excited forms of metallic molecules in combustion. The most likely molecular band emissions are from the excited states of metal oxides or metal hydroxides formed by these metals in the presence of the oxygen flow of the hybrid rocket. As the concentration of metallic dopants increases in the flame, the molecular band emissions also increase. The fashion by which they increase is observed here.

The high concentrations observed for these metals result in intensity versus concentration curves that diverge from the expected linear progression for manganese, magnesium and strontium. The molecular band emissions observed for calcium, barium and copper in this study followed linear progression, as does the atomic line emission for barium. The line emissions for manganese, strontium and calcium lean toward the concentration axis. The curves are attributed to selfabsorption or increased interactions among mixing species as metal concentration increases in the plume. This study indicates that molecular bands are useful for monitoring engine health and for plume diagnostics.

Keywords: combustion diagnostics, hybrid rocket, plume emissions, spectral signature, rocket exhaust, atomic spectroscopy, molecular spectroscopy, emission spectroscopy

Introduction

Atomic spectral techniques have been used in the past to provide diagnostics for engine health monitoring. The National Aeronautics and Space Administration (NASA) and Stennis Space Center in particular have taken interest in these studies as engine monitoring techniques for the Space Shuttle Main Engine (SSME).^[1–4] These techniques depend on the relationship of excited atomic species in the motor plume to the amount introduced by failures in the engine system. It is important that a linear or otherwise describable and reproducible relationship exists, to quantify wear or other elemental introduction factors in the motor or engine system.

Molecular emissions as observed in the normal realm of atomic spectroscopy are viewed as interference. A classic example is that encountered with analysis of barium in the presence of calcium.^[5] The analytical atomic line of barium is swamped by the presence of an overwhelming molecular emission from calcium, such as CaOH. Steps are usually taken to minimize the presence of these molecular bands in such work. However, these type precautions are not applicable to the field of engine health monitoring or in combustion diagnostics when applied to exhaust plumes. Molecular emissions are present in rocket combustion and should be factored in where quantitative data are required. A thorough study of the effect of molecular emissions in exhaust plumes is necessary to determine interference. fraction of species present as molecular versus atomic and other parameters.

The Hybrid Rocket Facility at the University of Arkansas at Little Rock (UALR) was constructed to provide combustion diagnostic testing and uses a 2×10 -inch labscale hybrid thruster.^[6,7] Previous studies have revealed the usefulness of the labscale hybrid rocket system as a plume simulator for other propulsion systems and characterized it for both atomic and molecular emissions.^[8–11] The presence of metallic molecular bands was noted in these studies, both from the combustion of HTBP fuel and as formed by metallic dopants, such as manganese.

To study the molecular bands in rocket plumes, the labscale hybrid rocket fuel was doped with various levels of metallic salts. Combustion of these salts results in band emissions attributed to metal oxides or metal hydroxides. Some of the metals were chosen due to their presence in alloys used in certain engine components and because they appear to have produced molecular bands in previous combustion studies.^[8,10–13] Other metals were added to the study based on their tendency to oxidize easily, thus being likely to produce refractory particles in combustion. Fuel grains were made using R-45 HTPB resin and Desmodur N100 curative. HTPB was placed in the mixing container and the amount of dopant was added. Then, N100 curative was added to begin the process of polymerization. The container was placed on the mixer between each addition. No plasticizers or other additives were used in this study. Previous work^[8-11] indicated that mixing was sufficient to ensure a reasonably homogenous fuel grain.

Conversion Units

1 lbm = 1 pound mass = 454 grams 1 lb = 1 pound = 454 grams 1" = 1 in. = 1 inch = 25.4 mm

Experimental

The University of Arkansas at Little Rock labscale hybrid rocket motor, designed for combustion diagnostics, was used in this study. The twoby ten-inch fuel grains for the rocket are produced on site, which allows for seeding the fuel to produce desired spectral emissions. This is accomplished by doping the fuel with metallic chloride salts. Table 1 lists the chosen metals and the salts used in the study. The table also indicates the percent metal component for each salt.

The procedure used to calculate the amount of dopant necessary to produce the desired concentrations of metal in the plume has been documented.^[13] The equations used are based on total

Table 1. Percent Metal Used in Study.

Metal and Symbol	Salt Dopant	Metal (%)
Magnesium, Mg	MgCl ₂ •6H ₂ O	11.95
Calcium, Ca	CaCl ₂ •2H ₂ O	27.26
Barium, Ba	BaCl ₂ •2H ₂ O	56.22
Copper, Cu	CuCl ₂ •2H ₂ O	38.18
Strontium, Sr	SrCl ₂ •6H ₂ O	32.86
Manganese, Mn	MnCl ₂ •4H ₂ O	27.76
Aluminum, Al	AICI ₃ •3H ₂ O	11.175

mass flow of the system during firing. These studies use an oxygen mass flow of 0.100 lbm/s. At this flow, the total mass flow is found to be 0.1344 lbm/s.

Initial emission studies indicated the capabilities of the rocket to produce emissions of metallic atomic and molecular species. Quantification studies have thus far focused only on the metal atomic emissions.^[12,13] The goal of this study was to determine feasibility to quantitatively characterize molecular band emissions based on relative emission intensity.

The emission detection system consisted of a quartz collection lens with a 100 mm focal length placed 20 inches (510 mm) from the exhaust plume axis and 6 inches (152 mm) behind the exit nozzle plane of the rocket motor. A black metal tube housed the lens used to focus the plume emissions onto the entrance slit of a SPEX 270M spectrometer. The entrance slit was set to different widths for the various species observed, specified by trial during initial metal firings. The spectrograph utilized a grating capable of spreading incident light in a 150 nm window onto a 1024 pixel silicon photodiode array (PDA). A portable computer was used to collect the PDA output. Figure 1 is a sketch of the data



Figure 1. A sketch of the optical setup used.

collection setup. This spectrograph has been described previously.^[14]

The 488 nm line of an argon ion laser was used to wavelength calibrate the spectrometer. The laser intensity was minimized and the beam was focused onto a nearly closed entrance slit to avoid damage to the photodiode array.

PDA detector scanning was initiated before firing and allowed to continue after shutdown to collect background scans, which were later subtracted. PDA scans were set to allow 100-ms time intervals for exposure. A total of 75 scans were collected for each experimental run. Each firing was programmed to last four seconds. Data was saved and transferred to a Pentium desktop PC for data reduction.

Data Analysis

Data was transferred to a desktop PC and the files were opened in WPLOT.^[16] The plots were transformed from "raw" PDA pixel plots to spectra with the correct wavelength scale by simply applying a scaling factor. From the dispersion of the grating spectrometer, 150.99 nm was covered in the spectral window of the spectrometer (i.e., the 1024 pixels of the PDA). Therefore,

$$\frac{150.99 \text{ nm}}{1024 \text{ diodes}} = 0.14706 \text{ nm/diode}$$

Each raw data point was multiplied by this factor, and the center wavelength of the window was used to provide a base point, or offset value. Application of the offset value resulted in a corrected *x*-axis with accurate wavelength values. Scans could then be displayed as regular two-dimensional or as three-dimensional plots. WPLOT provided that the data could then be saved as an ASCII file providing intensity vs. wavelength information for further post-processing as desired.

In reviewing the three-dimensional plots, it is obvious that the files show a distinct combustion initiation and post combustion period. The scans collected between these regions represent the stable combustion condition experimental run and are used for intensity versus metal concentration evaluation. This is consistent with previous studies.^[6–9] The combustion initiation period shows a gradual increase in flame emissions. Very intense emissions are seen in the post combustion scans. These intense emissions are explained as blackbody emissions that occur during oxygen shutoff. Once the oxidizer flow has stopped, combustion in the chamber goes into a fuel rich condition before extinguishing.

The plot files were all opened in Microsoft Word to remove scans from combustion initiation and post combustion. The resulting text files of X wavelength and Y relative intensity data sets, corresponding to wavelength versus intensity, were saved and reopened in Microsoft Excel. The X data set remained constant. The Y data sets were averaged to obtain a single plot. The average plot obtained from an undoped fuel grain was used to subtract basic combustion emissions from the averaged plot of a metal study. This helped to provide a more clear representation of metallic emissions. These plots were compared for different concentrations of metallic dopants.

Results

A basic spectrum was collected for the UALR hybrid rocket using several undoped fuel grains. The consecutive firings were centered on different wavelength windows within the ultravioletvisible region. The data were compiled, averaged and placed end-to-end for one continuous plot over the region of 200–800 nm. The figure starts at 250 nm. To see the combustion bands more clearly, the scale of intensity could be changed. Figure 2 is the result. This plot was used for identification of combustion products in the hybrid rocket plume. As expected, there were an abundance of hydrocarbon bands, plus the sodium and potassium atomic line emissions.



Figure 2. Combined hybrid rocket spectrum collected from 3 separate plain HTPB firings.

These line emissions were expected as they have been detected and identified as impurities in the rocket fuel materials.^[3,11] The sodium line emission appears at 589 nm as an unresolved doublet. Potassium appears as a doublet centered at 767 nm. In the discussion below, spectral data as normally seen in the lab is compared with that seen in the plume.

I. Manganese

Manganese is a metal used in alloys for valves and flex joints in NASA's Space Shuttle Main Engine (SSME). During combustion, it is known to produce a strong atomic line emission at 403.3 nm. This is actually a triplet. It also produces a strong molecular band system centered at 560 nm. This is thought to be due to manganese hydroxide (MnOH).^[14]

The plume emissions of HTPB doped with manganese chloride were monitored from 475 to 625 nm to evaluate the molecular band of manganese at different concentrations. Figure 3 shows an averaged scan for a manganese firing. The expected molecular band appeared at 560 nm. Firings were repeated with new fuel grains at increasing concentrations of this metallic salt. After collecting data for the molecular band of manganese, the wavelength selector was shifted to look at the atomic line emissions for this element, requiring a different wavelength window. Figure 4 is a typical manganese atomic line emission and appears at 403.3 nm as expected.



Figure 3. Manganese spectrum for 500 ppm Mn firing at 560 nm.

The evaluation for the atomic line emission intensity versus metal concentration coincides with earlier work.^[11] The curve bends toward the



Figure 4. Manganese atomic line emission for 100 ppm at 403.3 nm

concentration axis as concentration is increased (Figure 5). The nonlinearity for the atomic line emission with the increase in concentration can be attributed to self-absorption effects. At high concentrations, a significant fraction of photons emitted by atoms in an excited state are absorbed by atoms in the lower, ground state.^[16] This results in a bend in the curve toward the concentration axis.



Figure 5. Manganese atomic line intensity versus metal concentration.

Note that the atomic line emission for Manganese exhibits a flat top. This is also characteristic of high concentrations of analyte species and self-absorption. At low concentrations, the line emission will grow by increasing "normal" peak intensity, but at higher levels these emissions are self-absorbed by other atoms in the ground state. The center of the line profile will thus widen as the concentration is increased, resulting in this characteristic emission peak shape. Also possibly contributing would be the rather wide entrance slits used in the study, somewhat decreasing the resolution of the spectrometer and making the lines appear broader.

In comparing the atomic line curve to the molecular band curve, we find that the increase in concentration affects the molecular band curve differently. Figure 6 shows the effect of molecular band intensity for increasing concentration. The result is a roughly exponential increase in intensity. With such large increases in concentration, there are more collisions created by the metal radicals in combustion. This leads to an increasing fraction of molecular formation and therefore more likely excitations of the molecular species.

II. Copper

Copper is used in several alloys in the internal components of the SSME. During combustion, it is known to produce two strong lines at 324.7 and 327.4 nm. The compound CuH has been identified as the cause for the band head at 428.0 nm. Copper hydroxide (CuOH) has been found to produce the band systems from 535 to 555 nm and 615 to 625 nm. Well-defined band systems at 605 and 615 nm have been attributed to copper oxide (CuO).^[14]

The copper line emission was expected at 324.7 and 327.4 nm. Neither line appears. Previous studies did indicate the copper lines, but very weakly.^[11] Since the same motor combustion parameters were used in this study (0.100 lb/sec oxygen flow and HTPB), the differences in spectral collection would be indicated as a possible cause for this behavior. Indeed, the use of the wider entrance slit in this work would mask out a very low intensity emission such as that seen previously for copper, as it would not be resolved above the noise baseline/background signals. While self-absorption would also be likely at these concentrations (100 to 600 ppm), the root cause for not being able to see the weak atomic lines for copper is most likely spectrometer setup.

In further analysis, the molecular band emissions of copper are not very intense emissions. The molecular band emissions due to CuH are evident in Figure 7 at 428, 435, and 444 nm. Figure 8 shows the band emissions attributed to CuOH from 535 to 555 nm and from 615 to 625 nm. The CuO band also appears from 605 to



Figure 6. Manganese molecular band emission intensity versus metal concentration.

615 nm. One can note the sodium line emission at 589 nm as a sort of "landmark" for this study, as it is always present.



Figure 7. Copper molecular band emissions number 1 for 600 ppm Cu at 390 nm.



Figure 8. Copper molecular band emissions number 2 for 600 ppm Cu at 550 nm.

The intensity versus concentration for the molecular bands was evaluated and is reported in Figure 9. There is a linear relationship for the increase of intensity with increase in concentration. This suggests less fractional increase of molecular formations with increasing concentration, or closer to a constant proportionality of molecular formation.



Figure 9. Copper molecular band intensity versus metal concentration.

III. Alkaline Earth Metals

The next four metals studied were members of group II-A of the periodic table, the alkaline earth metals. These metals produce flame spectra that have overwhelming molecular bands and much less intense atomic emissions. In fact, it is not uncommon for over 90% of the emissions for these metals to be in the molecular form.^[15] Though this is usually the case, the most prominent line emissions for each element results from the transition between the lowest excited electronic state to the ground state. As such, all of these transitions produce singlets.

The atomic line emissions of these elements are dependent on temperature. Higher temperatures produce more atomic species and therefore more intense line emissions. Molecules dissociate at higher temperatures thus decreasing the intensity of molecular band emissions.

Magnesium

Magnesium produces its most prominent resonance line at 285.2 nm. Molecular bands appear between 353 and 415 nm. The two large band heads peak at 371 and 383 nm are both thought to arise from manganese monohydroxide, Mg(OH).^[15,18] The existence of MgOH is favored at lower flame temperatures. The thermal decomposition of MgOH causes the relative intensity of the atomic line emission to increase at higher temperatures.^[15]

The molecular bands at 371 and 383 nm, thought to be due to magnesium hydroxide, Mg(OH), can be seen in Figure 10. The intensities of the bands track together for changes in concentration. The figure also shows the absence of the magnesium atomic line emission at 285 nm. This indicates that metal exists in molecular form in the plume, as may be expected.



Figure 10. Magnesium molecular band emissions at 320 nm.

Figure 11 is the intensity versus concentration for the magnesium molecular band. The two bands were treated separately for this relationship. The upper line is the calibration curve for the molecular band seen at concentration. Like manganese, this indicates an increase in molecular formation with an increase in concentration. This behavior may be due to the change in thermal activity within the flame at different concentrations of metal. Higher analyte concentrations



Figure 11. Magnesium molecular band emissions versus concentration, 371 and 383 nm bands.

will lead to an increase of interactions and thus a higher rate of metallic molecular formations. Therefore, the emission intensities for these bands will increase with the concentration of the metal in the fuel.

Strontium

The strontium molecular band systems make up the majority of the flame spectrum. The narrow band head at 606 nm and a wider system from 640 to 700 nm arise due to strontium monohydroxide (SrOH). The band heads in the wider system are seen at 650, 668 and 683 nm under conditions of narrow slit widths. Wider slit widths result in smoothing of that system into one large band. The last band system, near 595 nm, has been identified as arising from strontium peroxide (Sr₂O₂). Molecular band systems are favored in cooler flames.^[14] The small strontium atomic line is found at 460.7 nm. In very hot flames, the strontium atom can be ionized to produce a doublet at 407.8 and 421.6 nm.^[15,17] The hybrid rocket plume is not hot enough to produce these lines, and Figure 12 shows the resulting spectrum (Sodium at 589). The atomic resonance line of strontium also appears at 460.7 nm (Figure 13).



Figure 12. Strontium molecular band emissions for 200 ppm Sr at 650 nm.

Strontium molecular band intensities were plotted versus concentration in Figure 14. There is a slight bend toward the concentration axis as the concentration is increased. This is like the intensity versus concentration for the atomic line emission (Figure 15). This relationship is attributed to self-absorption of the molecular emitting species with high concentrations of analyte.



Figure 13. Strontium atomic line emissions for 220 ppm Sr at 460 nm.



Figure 14. Strontium molecular band emissions versus metal concentration.



Figure 15. Strontium atomic line emission versus metal concentration.

Calcium

The calcium resonance line arises at 422.7 nm. When calcium is singly ionized it will produce a doublet at 393.3 and 396.8 nm. This only occurs under extremely high-energy conditions not attained by the hybrid rocket plume. Most of the calcium emissions result in two large band systems attributed to calcium oxide, (CaO), and calcium monohydroxide, (CaOH). The narrow green system stretches from 547 to 560 nm with a band head at 554 nm. The wider dark orange system extends from 580 to 650 nm with two band heads at 606 and 622 nm, when a narrow slit width is employed.^[15, 19] The total emissivity of calcium increases with flame temperature. However, the relative intensities of the molecular species versus atomic and ionic species shift away from the molecular systems at higher temperatures. The higher number of atomic species formed by dissociation at the higher temperatures creates a larger probability for atomic excitation and ionization.^[15]

The large molecular bands produced by the dopant are shown in Figure 16. The calcium oxide (CaO) system a 547 to 560 nm is the tall and narrow system. The wider system from calcium hydroxide (CaOH) is seen from 580 to 650 nm. The band heads in this system appear at 606 and 622 nm as anticipated. The calcium line emission at 422 nm was collected separately (Figure 17). Unlike some metals in this study, the atomic line emission is within the 150 nm range of the narrow band emission at 554 nm. The two systems were collected in one scan. The narrow band emission is a common structure in both series of firings, which can be used to "calibrate" and compare one spectrum to the other.



Figure 16. Calcium molecular band emission for 400 ppm Ca at 590 nm.

Calcium molecular band intensities versus concentration are plotted in Figure 18. The result is a linear relationship. In evaluating the trend in atomic line emission with increasing concentration, the atomic line emission was found to be relatively constant in intensity. The plot of atomic line intensity versus concentration (Figure 19) appears to have leveled off. It is suspected that



Figure 17. Calcium atomic line emission for 400 ppm Ca.

at the high concentrations evaluated here, the atomic species are self-absorbing radiation while the analyte is preferentially forming molecular species.



Figure 18. Calcium molecular band emissions versus metal concentration, 554 and 622 nm bands.

Barium

Barium produces a much less intense spectrum than other alkaline earth metals. The atomic resonance line arises at 553.6 nm between the barium oxide bands. When barium is ionized, a doublet appears at 455.4 and 493.4 nm. Unlike spectra from other alkaline earth metals, the molecular systems directly surround the atomic line emissions. Barium monohydroxide (BaOH) produces relatively strong molecular bands at 487, 515, and 527 nm. Weak bands arising from barium oxide (BaO) stretch from 530 to 630 nm.



Figure 19. Calcium atomic line emission versus metal concentration.

Experimentally, the molecular bands and the atomic line emissions for barium are produced in the same data collection scan. Figure 20 illustrates the barium spectrum. The atomic resonance line at 553.6 nm is prominent among the barium oxide bands that range from 530 to 575 nm. Barium monohydroxide (BaOH) bands also appear from 480 to 530 nm.



Figure 20. Barium atomic line and molecular band emissions for 525 nm.

The plot of barium emission intensities versus concentration appears as Figure 21. Both the atomic line and molecular band intensities produce a linear increase with concentration. Furthermore, the atomic line trend is almost parallel to the molecular band trend. This suggests that the atomic and the molecular species for barium exist in a definite proportionality during combustion.



The barium molecular emissions are of rather weak intensity when compared to other alkaline earth metals such as calcium and strontium. As a result, the atomic line emission seems to be of much higher proportionality. However, other metals do not produce molecular band emissions that spread across such a wide spectral region. This supports the tendency for alkaline earth metals to exist primarily in molecular form during combustion. Even at the high concentrations of analyte present in these studies, barium is not in high enough concentration elementally to show characteristics of self- absorption.

IV. Aluminum

Aluminum is known to produce several molecular band systems. Two in particular, arising from AlO⁺, should be seen at 435–500 nm and 508–518 nm, the most intense emission centered at 484 nm. The atomic line emission of aluminum should occur at 396.2 nm when flame temperatures are hot enough to allow aluminum to exist in the atomic form. The relative intensities of the atomic line versus molecular bands will vary depending on flame temperature. Higher temperatures will produce more atomic species as the molecules are dissociated. The atomic line emission intensities should rise as the molecular band emissions decrease.^[15,20]

Initial data collection of aluminum using 100– 1000 ppm aluminum concentrations produced no indication of molecular band or atomic line emissions. Because aluminum has such a high tendency to oxidize, it is thought that the aluminum in the presence of the oxidizer flow goes straight to a blackbody particulate, aluminum oxide (Al₂O₃). No useable data were collected.

Aluminum is known to scavenge magnesium during combustion. By burning grains having a constant concentration of magnesium while increasing the aluminum concentration, the decrease in magnesium intensity should be observed. This would provide information on the combustion of aluminum. Attempts to observe the decreasing intensity of the magnesium molecular bands with increasing aluminum concentrations failed. There was no observable change. No background emission changes (i.e., blackbody emissions) were observed either. Aluminum emissions remain a mystery.

Note that there was a definite build-up of silvery material, perhaps aluminum metal, on the nozzle after these firings. This suggests that the metal partly exists in the elemental form at least in the chamber, but may not be excited, as the rocket combustion temperature is not hot enough. Transformation into the oxide after being forced through the nozzle may not actually occur until further into the length of the plume, due to possible after-burning of these particulates. It can be noted that aluminum oxide often coats the divergent side of a nozzle with a whitish and ragged coating.

Conclusions

Plumes containing high concentrations of metals were monitored for their emissions in this study. Most of the metals behaved generally as expected (i.e. a linear increase in molecular band emissions was found with increasing concentration). However, it appears that this behavior has many limitations. Self-absorption of emitting species appears to plays an important role in the characterization of these metals by molecular emission. Another important factor seems to be the molecular interactions among the metallic molecular species with increasing density in the plume. Together, these two limitations help to explain the unexpected behavior of the metals observed.

Manganese and magnesium exhibit an increase in fraction of molecular band emissions as metal concentration in the plume is increased. This may result from increased interactions among analyte species with flame gasses and each other.

Copper, magnesium and aluminum resonance line emissions were absent entirely. This was quite unexpected for the copper study, as copper is known to exist primarily in the free atomic form during combustion. It was not so unexpected for the magnesium and aluminum studies. Magnesium, an alkaline earth metal, is known to exist primarily in a molecular form in combustion. Aluminum, which also oxidizes readily in air, was expected to exist in the molecular form as well. Its molecular band emissions were not detected.

Alkaline earth metals exist primarily in the molecular form during combustion. Calcium and barium indicate a clear linear increase in molecular band intensity with increasing metal concentration. Strontium, on the other hand, exhibits characteristics of self-absorption for both the atomic and molecular species observed. The deviation from linearity occurs with a bend toward the concentration axis with increase in metal concentration.

The high concentrations evaluated for these metals resulted in unexpected intensity curves observed for atomic line and/or molecular band emissions. This is a safety concern for plume health monitoring. Unknown concentrations of metal, especially at higher concentrations, may provide misleading information of the amount of metal present in the plume. Therefore, the amount of component degradation for materials in the engine combustion path could be underestimated. The hybrid rocket proves to be a reasonable source for molecular emission quantitative studies. It allows for the development of techniques to evaluate metals and characterize their molecular formations during combustion. These results can be applied to larger hybrid rockets enabling the further generation of hybrids as possible flight propulsion systems.

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