Investigation of High Pressure Solid Propellant Combustion Chemistry Using Emission Spectroscopy

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A survey of the chemiluminescent emission in the range from 280 and 800 nm from the flames of ammonium perchlorate (AP)- and HMX-based solid propellants has been performed at pressures from atmospheric to 7 MPa (1000 psig). The AP propellant flame showed the emission of CH, CN, NH, and OH at atmospheric pressure (under nitrogen), as well as emission from several trace impurities such as Na, K, and Ca. As the pressure was increased, the banded molecular emission of all molecules except OH was rapidly obscured by a continuum that spanned the range 350-550 nm. In contrast, the HMX propellant showed CN, NH, and OH emission at pressures up to 7 MPa. CH emission was not detected in the HMX flame at any pressure; C_2 emission was not detected in either propellant flame. Spatial intensity distributions of emitting species were obtained, showing OH and atomic emission spatially distributed throughout the propellant flame and CN and NH emission confined to the region near the surface.

Introduction

CURRENT solid propellant combustion models have several limitations which can restrict their usefulness to the propellant formulator or rocket motor designer.[1] The models tend to emphasize the thermophysical aspects of solid propellant combustion at the expense of chemical detail. A more detailed model of the propellant flame chemistry will be important in understanding the often large effect that small changes in propellant formulation (such as a change in curative) can have on propellant combustion behavior. More powerful combustion models that link gas phase chemistry to propellant performance will require more detailed chemical kinetic information about solid propellant flames than is presently available.[1] Spatially and temporally resolved species concentration and temperature profiles will be necessary to construct these models. The most promising means of obtaining such data are the recently developed nonintrusive laser optical combustion diagnostic techniques, such as laser-Raman scattering and laser-induced fluorescence (LIF).[2,3]

The use of combustion diagnostics in solid propellant flames is made more difficult by the complex nature of the flames. For example, the "flame" above an ammonium perchlorate (AP)-oxidized propellant is actually a combination of several flames: the oxidizer decomposition (monopropellant) flame, the primary (oxidizer/binder) flame, the energetic binder flame (if any), and the final flame.[1] The relative importance of these flames depends on the oxidizer particle size, nature of binder, and pressure. Low pressure (atmospheric and below) AP propellant flames tend to resemble a premixed flame with little binder or particle size influence. As pressure increases, diffusion is retarded and reaction rates are enhanced leading to diffusion flames between oxidizer and binder. These primary diffusion flames are strongly influenced by binder type and oxidizer particle size. At much higher pressures, the reaction rates have been accelerated so much relative to diffusion rates that the AP monopropellant flame begins to control the propellant burn rate.[4] In contrast, HMX propellants tend to have less interaction between HMX decomposition products and binder, primarily because HMX is not oxidizer rich. Experimental results support this observation. For example, the burn rate of HMX propellants is generally only weakly dependent on HMX particle size.[1,5] The addition of AP to HMX propellants was seen to change the flame structure dramatically by introducing oxidizer/binder diffusion flames, while the reverse was not true.[6] Thus, the flame chemistry in solid propellants is more complex than that usually seen in laboratory gas flames. Ideally, solid propellant flame diagnostics must be able to temporally and spatially resolve chemistry on the scale of oxidizer particle sizes and burn times, since the flame chemistry (at least for AP composite propellants) changes at a given point above the surface as oxidizer particles are uncovered and consumed. In the initial stages of a program to obtain the detailed chemical information needed for improved solid propellant combustion models, the structure of several different solid propellant flames was studied using emission spectroscopy at pressures from atmospheric to 7 MPa (1000 psig).

Emission spectroscopy of solid propellants is not a new field of research. Emission spectra have been published for double-base propellants[7-9] and several different AP-based composite propellants.[10-14] In general, few reactive radical species were seen in emission in double-base propellant combustion because continuous emission generally filled the spectral regions of interest, especially at pressures above atmospheric. Similar problems with continuous emission were encountered in AP-based composite propellants. "Clean" spectra could be obtained with atmospheric pressure propellant flames, showing C_2, CH, OH, NH, CN, and NO (γ system), but continuous emission rapidly replaced or obscured the emission of these species at pressures above approximately 0.5 MPa (70 psig).[10,12] The strength of the continuum was found to be a function of binder type and AP particle size. The continuum is generally attributed to the CO + O recombination,[11] although the spectral distribution found in shock tube studies of the CO + O reaction is somewhat different than that seen in these propellant experiments at similar temperatures.[15]

It must be emphasized that emission is not, in general, correlated with the overall concentration of the species. Emission is proportional to the concentration of the chemically excited

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Received Aug. 15, 1985; revision received Jan. 6, 1986.

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state of the species, which is generally a small fraction of the overall species concentration. Thus, the species distribution shown by emission would generally be different from that shown by LIF, which measures the unexcited (ground) state distribution. Due to fast quenching times, the excited state population should be confined to the region of the flame where it was formed. Thus, emission spectroscopy can be used to locate reaction zones, although it must be kept in mind that the reactions forming the excited species may be minor channels in the overall chemistry of the species. Several previous attempts to characterize the structure of propellant flames used emission from highly reactive radicals such as CN as a characteristic of the "primary reaction zone." At atmospheric pressure, the spatial extent of the primary reaction zone was apparently quite variable, ranging from less than 500 μm to 2000 μm.[10,12,14] The reaction zones are much larger than the primary reaction zones used in current solid propellant combustion models, which range from approximately 1-100 μm.[16-21] It must be noted that a comparison of the "flame sheets" used in the combustion models and the columnar diffusion flames thought to be present in the propellant flame is inconsistent. Also, atmospheric pressure flames may have an appreciable premixed character, which disappears in the pressure range of interest, complicating the interpretation of the atmospheric pressure data.

In addition to flame structure, emission spectroscopy can also give some information about flame chemistry by a comparison of the propellant flame emission and the emission from known flames. The combustion chemistry of AP and HMX propellants has been the subject of many studies, although most chemical detail comes from experiments at conditions far different from those encountered during combustion in rocket motors. Ammonium perchlorate burning as a monopropellant is thought to dissociate into NH_3 and $HClO_4$, with $HClO_4$ quickly decomposing into ClO, OH, and O_2. The ammonia is subsequently oxidized by the very reactive ClO and OH radicals in a premixed flame.[22-25] At low pressure, a similar premixed flame would be formed with binder pyrolysis products as the fuel. At higher pressures, the AP/binder flame would become a diffusion flame. Premixed $HClO_4/CH_4$ flames have been studied at low pressures,[23,24] showing OH, CH, and C_2 emission and no ClO emission. Premixed NH_3/O_2 flames have also been examined, showing OH, NH, NH_2, and NO + O emission.[26] However, the chemistry (and thus the emission) from diffusion flames is quite different. In a hydrocarbon/oxygen diffusion flame, the initially unmixed fuel and oxidizer are separated by combustion products.[27] The fuel generally pyrolyzes significantly before it has diffused into the reaction zone, with C and H_2 from this pyrolysis reacting with the oxidizer in the reaction zone. This type of flame does not show the CH and C_2 emission from the reaction zone seen in premixed hydrocarbon/oxygen flames. Thus, the obscuration of the molecular emission discussed in the preceding paragraph may be due to the transition from a low pressure premixed propellant flame to a higher pressure diffusion-controlled flame. It is apparent that the relevance of premixed flame data to propellant flames controlled by diffusion is tenuous.

The HMX flame is thought to occur as a breakup of the cyclic nitramine molecule into smaller fragments, such as CH_2O and HCN (fuels) and N_2O and NO_2 (oxidizers), with these species then forming a premixed flame above the propellant.[19-21,28,29] The emission from premixed flames with N_2O and NO_2 as oxidizers varies dramatically depending upon the fuel.[26,27,30] Flames with CH_2O as the fuel show OH, NH, and NH_2 emission, but no C_2, CH, or CN emission. In contrast, hydrocarbon/NO_2 and N_2O flames show emission from OH, C_2, CH, CN, NH, and NH_2. The relative intensity of the emission is a strong function of the nature of the hydrocarbon and the mixture ratio. For example, rich flames and carbon-rich fuels generally show much stronger C_2 emission than lean flames of hydrogen rich fuels (e.g., CH_4). Thus, the flame emission can give some clues to the chemical processes occurring in flames.

Experimental Approach

To investigate the gas phase chemistry of solid rocket propellant, an environment that simulates the conditions inside a solid rocket motor as closely as possible is desirable. In this research, the high-pressure conditions in a motor are approximated by burning strands of propellant in a nitrogen-purged high pressure combustor. Optical access is provided by four 3.8 cm diameter sapphire windows. The height of the burning surface of the propellant is kept constant relative to the optical system by a servo-positioning system which elevates the strand as it burns, using a spatially fixed He-Ne laser beam as a reference. The radiant emission from the combustor is collected, collimated, and focused on the entrance slit of a spec-

Table 1 Summary of propellants used

	HMX propellant	AP propellant
Ingredient, wt %		
HMX	73	0
Polyester binder	10	0
TMETN	17	0
AP	0	87
Polybutadiene binder	0	13
Impurities, by analysis, ppm		
Na	100	300
K	10	100
Ca	20	400
Fe	30	na
Cr	1	na
Equilibrium species at 3.5 MPa, mole %		
CO	34.5	11.1
CO_2	4.7	11.6
Cl	0.0	1.3
HCl	0.0	17.7
NO	0.0	0.2
N_2	24.0	9.5
H	0.3	0.6
H_2	19.3	5.4
H_2O	17.1	40.8
O	0.0	0.1
OH	0.1	1.4
O_2	0.0	0.3
T (adiabatic), K	2620	2970
Burn rate, 3.5 MPa, mm/s	2.5	8

Table 2 Species seen in emission

	AP	HMX
Reactive radicals (transition; bands)		
OH (A-X; 0-0 and 1-0 sequences)	+	+
CN (B-X; 0-0, 0-1, 1-0 sequences)	*	+
NH (A-X; 0-0, 1-1)	*	+
CH (A-X; 430 nm system)	*	X
C_2 (A-X; 0-0, 1-0, 0-1 sequences)	X	X
ClO (A-X; 0-6, 1-7)	X	X
Trace Species		
Na (589.0, 589.6, 330.2-3 nm)	+	+
K (766.5, 769.9, 403.5, 404.4 nm)	+	+
Ca (422.7 nm)	+	+
CaCl (618.5, 619.3, 621.2, 622.5 nm)	+	X
CaOH (553.9-554.1 nm)	+	−
Fe (386, 387.9, 388.7 nm, etc.)	X	+
Cr (425.4, 427.5, 428.4 nm)	#	+
Ni (lines from 337-353 nm)	#	#
Mg (285.2 nm)	X	+
Sn (284.0, 286.3 nm)	X	+
Cu (324.8, 327.4 nm)	X	+

Note: + = observed at all pressures; * = observed only at low pressure; X = not observed; and # = observed only during ignition.

trometer by a pair of lenses. The collimated image of the flame is rotated 90 deg by a set of mirrors so that, in effect, the vertical entrance slit of the spectrometer is projected horizontally on the propellant flame. The resulting image is thus a horizontal average through the flame. The Spex Triplemate Model 1877 spectrometer disperses and projects the flame image onto an EG&G/PAR 1240 Reticon diode array detector (700 pixels), controlled by an EG&G/PAR OMA II detector controller and data acquisition system. This system allows variable signal integration time and the collection of multiple data scans of a fixed spectral region.

The advantage of this type of system over a scanning monochromator is that broadband spectral information can be collected on a time scale of tens of milliseconds rather than minutes, with obvious advantages for short duration solid propellant combustion studies. The speed with which resolved spectra can be taken is a definite advance over previous methods which employed photographic detection.[3] The optical collection system is aligned using a He-Ne laser similar to the laser that controls the position of the strand surface. The vertical difference between the two beams defines the height of the data collection region above the propellant surface. Tests have indicated that the resolution of the optical system (dependent upon the entrance slit width of the spectrometer and the lens/mirror combination used) ranges from 100 to 500 μm for the results reported here. Typically, strong emitters such as Na and OH could be resolved to 100-200 μm, while CN, CH, and NH could be resolved to only 500 μm.[31] This large collection volume is necessary in emission spectroscopy to obtain sufficient signal-to-noise ratios. One of the advantages of laser-based spectroscopies is that much greater signals are generated in a given volume and thus these techniques can behave correspondingly greater spatial resolution. Emission spectroscopy is also limited in that it is a line-of-sight integration of the emission over the entire depth of the flame, thus only one-dimensional variations in intensity above the surface can be investigated.

The propellants described in this paper are listed in Table 1. Comparison of the adiabatic flame temperatures of the monopropellants (AP: 1428 K, HMX: 3228 K, TMETN: 2824 K at 3.5 MPa) with the propellant flame temperatures illustrates the differences between the two propellants. The AP monopropellant flame is relatively cool with a flame temperature half that of the propellant. Thus, the interaction of the AP and binder is quite important to the propellant combustion processes. In contrast, the addition of binder products to the already fuel-rich HMX lowers the flame temperature. Thus, the diffusion of excess oxidizing species from the HMX monopropellant flame to a primary oxidizer/binder flame is unlikely. Therefore, one would expect the HMX propellant flame to show more premixed character and the AP propellant flame to have a strong diffusion flame character at pressures of interest. A more detailed description of the experimental apparatus and procedures can be found in Ref. 31.

Results and Discussion

A survey of the emission from both AP and HMX propellants in the wavelength range 280-700 nm was performed in this study. The important variables investigated were pressure and height of collection volume above surface. This height (h) is defined as the height of the center of the 200-1000 μm thick collection volume above the surface. Thus, a height defined as $h = 1000$ μm with a resolution of 500 μm means that the chemiluminescent emission was collected from a region from approximately 750-1250 μm above the surface.

AP Propellants

The strength and character of the emission from the AP propellant varied strongly with pressure. At all pressures, the emission originated mainly from the trace impurities in the propellants (Na, K, Ca), combinations of the impurities with flame species (CaCl, CaOH), and OH emission. A continuum was also present in the wavelength range 330-550 nm, which increased rapidly in intensity as pressure increased. Only at the lowest pressures investigated could emission from CN, NH, and CH be detected. This emission was rapidly replaced by the continuum as the pressure increased above atmospheric, with the continuum totally replacing the molecular emission at

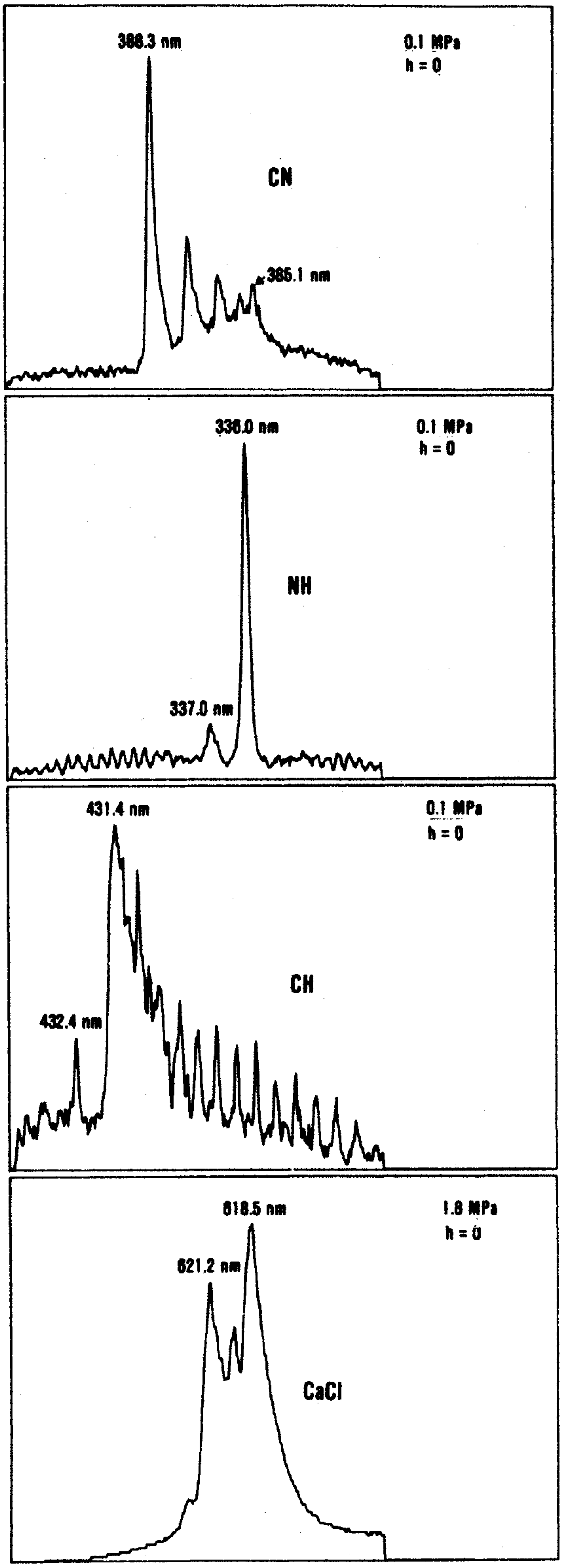

Fig. 1 AP propellant emission spectra, where h = height of center of collection volume above surface.

pressures above 0.5 MPa. These results are similar to those discussed in the introduction, and are summarized in Table 2 and Figs. 1 and 2. At 0.1 MPa (10 psig), the ratio of the highest peaks in the emission spectra of the important radicals was CN/OH/NH/CH = 7/6/5/1. No C_2 emission was detected. Because of the photoelectric (as opposed to photographic) detection system and higher resolution spectrometer used in this research, the spectra (notably OH, NH, and CH) are more highly resolved than those previously published.[7-14] However, individual rotational lines are not resolved.[33] For example , a series of OH emission spectra are shown in Fig. 2. The emission in this region originates from the 0,0 and 1,1 vibrational bands of the OH A-X transition. This OH emission is an ubiquitously feature of flames containing hydrogen and oxygen.[26] Analysis of this spectrum is complicated by incomplete resolution of lines, possible self-absorption effects, pressure broadening of lines, and an apparent pressure-dependent background[32,33]; however, some general observations can be made.

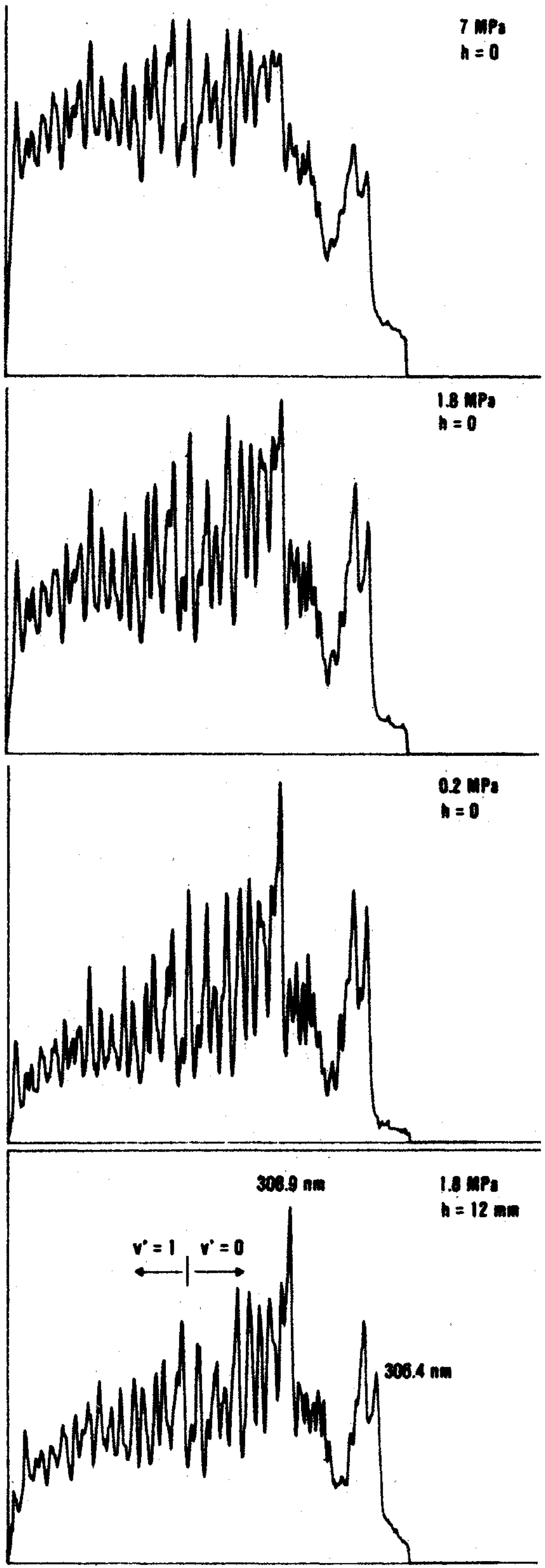

Fig. 2 Effect of pressure and distance above surface on OH chemiluminescence during AP propellant combustion.

The structure of the OH emission spectrum (and consequently the rotational and vibrational populations) appears to be a function of pressure and height above the propellant surface. This is evident in Fig. 2. Increasing the pressure and moving closer to the surface have a similar impact on a given OH spectrum, an apparent increase in the population of the $v' = 1$ vibrational level. Another notable point is the large distances from the surface at which significant OH emission is still seen. A more detailed analysis, with the calculation of approximate rotational temperatures, has been performed.[33] Models of AP-based composite propellants generally predict final flame heights on the order of 100-500 μm,[16,17] implying that the conversion of reacting molecules to final products should be complete outside this flame zone. The fact that OH emission is seen at such large distances from the surface at these pressures indicates that significant reactions involving OH are occurring even at 10 mm (0.4 in) from the surface and that a flame sheet is a poor approximation to the extended final flame. Because of the high quenching rates at pressures above atmospheric,[34] this OH emission is not due to reactions occurring closer to the surface and radiating at a later time and larger distance away from the surface. As can be seen in Table 1, there is an appreciable equilibrium concentration of OH at the flame temperature, although this is ground state OH and not the excited state OH that causes the chemiluminescence. In any case, OH emission is usually found throughout a flame,[26,27] so the OH molecule is a poor indicator of primary reaction zones. Recently acquired two-dimensional imaging of these propellant flames using a Vidicon two-dimensional detector tends to confirm the flame structure indicated by these results. The UV emission from the flame (primarily OH and the continuum) tends to show a broad emission intensity distribution with the strong intensity region extending many millimeters above the propellant surface. The visible image of the flame is of similar size.[35] For this reason, another molecule, such as CN, NH, or CH, would be a better indicator of reaction zones. However, the emission from these molecules is obscured by the continuum at pressures much above 0.1 MPa. Apparently, the monopropellant flame, which could show molecular emission (such as NH emission), does not create the right environment to yield much emission. Determining the structure of the AP propellant flame spectroscopically will require a diagnostic technique that will create a signal-to-noise ratio that is sufficiently large to overcome the background continuum at high pressures. Another consideration is that other types of spectroscopy will also allow observation of molecules that do not emit under the conditions in the propellant flame. Of course, it may be the case that the absence of emission from such molecules as CN and NH indicates that the diffusion flame is totally dominant and that these species do not exist in appreciable concentration in the AP propellant flame at pressures above about 0.1 MPa. This remains to be determined.

The distribution of emission from the species that do emit in the flame has been examined. In general, the emission from the impurities (Na, CaCl, etc.) and OH tends to rapidly increase above the propellant surface, reaching a maximum at 2-3 mm above the surface and extending out past 10 mm. At low pressures, the CN, NH, and CH emission behaves quite differently, generally reaching a maximum and dropping back to low levels within 2-3 mm. Again, at higher pressures the emission of CN, NH, and CH is absent. This is illustrated in

Figs. 3 and 4 where the emission intensities for each molecule are converted to a relative scale. The vibrational energy distribution in the CN molecule shows behavior similar to that seen in OH with the 4,4 bandhead at 351.1 nm ($v' = 4$) confined to a region much closer to the surface that the 0,0 bandhead at 388.3 mm. These intensity profiles were obtained by allowing the propellant to burn down through the collection volume, in essence allowing sequential data collection from progressively higher in the flame. The surface is defined as the point of first significant emission. There is no evidence in this data to support idealized flame models which show thin flame sheets at distances on the order of 100 μm for the final flame and 10 μm for the primary and monopropellant flames at typical pressures. If one assumes that the Na emission is a function of temperature, then the final flame, defined as the part of the flame that has reached the maximum flame temperature, is a rather large flame with a thickness on the order of centimeters. This is approximately the same size as the visible flame.

HMX Propellants

The emission from the HMX flame is quite different from the AP propellant flame in several ways (see Fig. 5 and Table 2). The molecular emission from CN and NH is seen at pressures up to 7 MPa (1000 psig). At 3.5 MPa, the ratio of emission intensities (maximum peak heights) is approximately CN/NH/OH = 5/1/1. No CH or C_2 emission was detected at any pressure (Table 2). The presence of molecular emission at the highest pressures implies that the HMX propellant flame shows much more premixed character than the AP flame. As already discussed, this is basically due to the fuel-rich nature of the HMX. The continuum is much weaker in the HMX flame, which is probably due to the smaller amount of oxygen in the flame (see Table 1). The combustion behavior of the

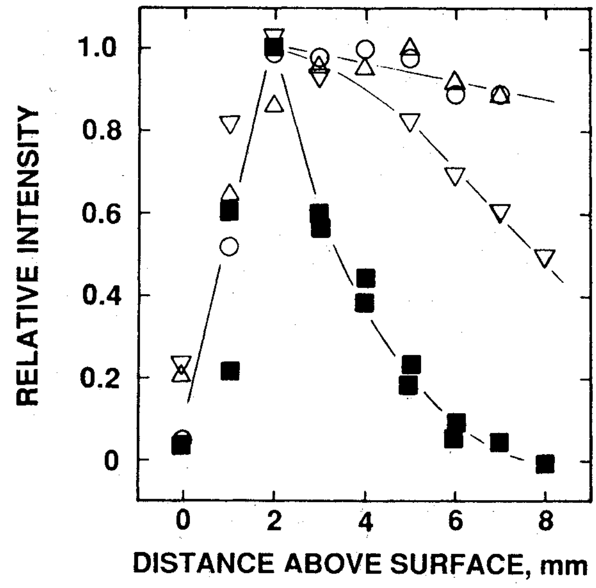

Fig. 3 Emission intensity as a function of distance above surface for AP propellant, 0.1 MPa [■ = CN (388.3 nm), ▽ = CaCl (618.5 nm), △ = Na (330 nm), ○ = OH (309 nm)].

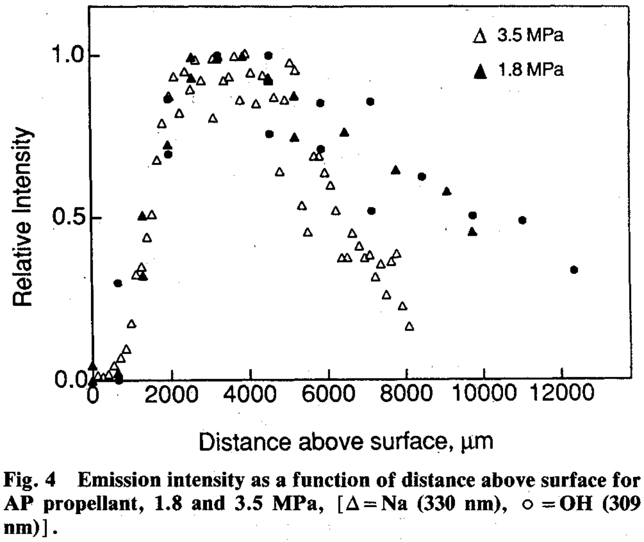

Fig. 4 Emission intensity as a function of distance above surface for AP propellant, 1.8 and 3.5 MPa, [△ = Na (330 nm), ○ = OH (309 nm)].

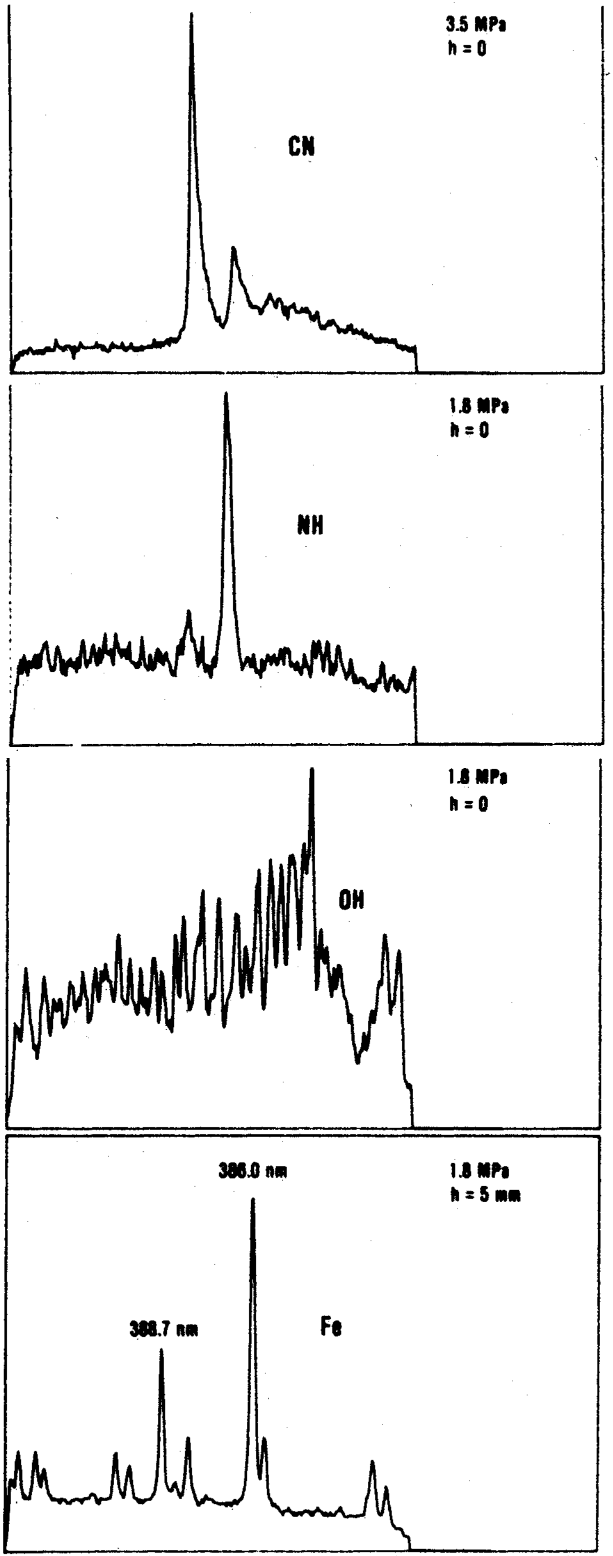

Fig. 5 HMX propellant emission spectra.

HMX propellants is significantly different from that of the AP propellants in another way. Unlike the AP propellants, the HMX propellants will not burn under nitrogen at atmospheric pressure. They will however burn quite well in air at atmospheric pressure, because of the diffusion of oxygen into the flame, which indicates that the combustion of HMX in air may be proceeding by a significantly different mechanism than the combustion of HMX in an inert atmosphere.

It is interesting to compare the emission seen in the HMX propellant flame to the emission seen in the flames of proposed intermediates in HMX combustion.[19-21,28,29] On the basis of low temperature decomposition studies, it has been suggested that the primary decomposition products of HMX are CH_2O ANd N_2O. CH_2O/N_2O flames have been studied,[30,36] with the primary emission species being OH, NH, NH_2. No CN, CH, or C_2 emission was seen. High temperature decomposition studies indicate that, under conditions more similar to propellant deflagration, HCN is a major product (along with NO_2). An HCN/NO_2 flame should (analogous to HCN/O_2 flames[37]) have CN and NH as intermediates, but not CH. Thus, it may be speculated that the strong CN emission and absence of CH emission is due to the predominance of HCN as the fuel species, at the expense of hydrocarbons or CH_2O. Note that the flame of the energetic plasticizer must also be considered. Multiply nitrated esters, such as TMETN, have been found to decompose into (mainly) NO_2 and aldehydes.[38] Aldehyde/NO_2 flames show no CN or CH emission, while hydrocarbon/NO_2 flames show both. Thus, the presence of the TMETN does not affect the observation of CN in the absence of CH emission. Our data, then, appears to confirm the importance of pathways other than CH_2O/N_2O in HMX propellant combustion. LIF measurements underway on CN and CH should give a much firmer basis for assignment of HMX flame reaction mechanisms.

Emission profiles for various species have been obtained in the HMX propellant flame at 3.5 MPa in the same manner as for the AP propellant flames. The main difference is CN and NH emission can be seen at these pressures in the HMX propellant flame. Typical emission profiles are shown in Fig. 6. The profiles are similar to those seen in low pressure AP propellant flames. The "primary reaction zone" (characterized by CN and NH emission) is quite extended for such a high pressure, extending over several millimeters. The data indicates chemistry involving CN and NH occurring on a scale of millimeters, larger than would be expected from current HMX propellant combustion models. The temperature profiles implied by the Na emission is similar to that found by Kubota, who used microthermocouples to follow the spatial variations in temperature in an HMX-based solid propellant.[28] These results, although not definitive because of the limitations of emission spectroscopy, are quite interesting, and the detailed study of the reaction zones in solid propellant flames using advanced combustion diagnostics that is now underway should yield important results.

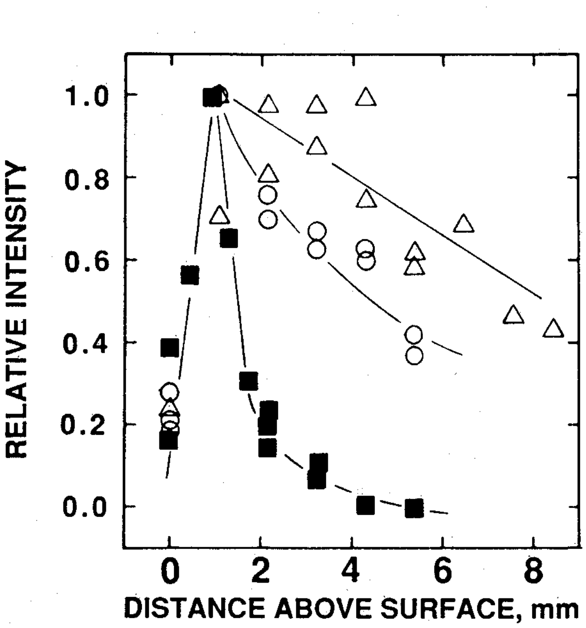

Fig. 6 Emission intensity as a function of distance above surface for HMX propellant, 3.5 MPa [■ = NH (336 nm), ○ = Na (330 nm), Δ = Cu (325, 327 nm)].

Summary

Emission spectra have been taken of AP and HMX propellant flames at pressures from 0.1 to 7 MPa (1-1000 psig). The AP flame emission was similar to previously published results, with strong continuous radiation (350 to 550 nm) at pressures above approximately 0.7 MPa (100 psig). At atmospheric pressure, CH, NH, and CN emission was detected, as was OH which was the only molecular emission of a chemically important species visible at the higher pressures. The HMX propellant flame showed much more structure at typical rocket motor pressures, with OH, CN, and NH emission identified at pressures up to 7 MPa. CH emission was not seen in the HMX flame, and C_2 emission was not seen in either propellant flame. For the HMX propellant flame, the CN and NH emission above the surface extended over several millimeters at 3.5 MPa (500 psig). This distribution was similar to that seen in AP propellant at pressures near atmospheric.

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