PROPELLANT DARK ZONE CONCENTRATIONS VIA MULTICHANNEL IR ABSORPTION

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A multichannel infrared absorption technique has been developed and applied to the study of steady-state, self-sustained combustion of solid propellant flames at elevated pressure. An infrared light source, windowed pressure chamber, and spectrometer-diode array detector formed the basic experimental setup with which in situ absorption measurements were made. Spectra were obtained over the wavenumber range of 2300 to 6000 cm^{-1}. Within this range, absorptions for HCN, H_2O, N_2O, CO, CO_2, and CH_4 have been detected through the use of a 1024-element platinum silicide array detector with the ability to read complete spectra in 10 ms. Experimental dark zone results for a nitramine propellant (XM39) and a double-base-like propellant (JA2) have been obtained, and these absorption spectra analyzed with a full spectrum, multivariate, nonlinear, least-squares-fitting pc program that makes use of the HITRAN database for the required molecular information. In some cases, the absorption spectra of the molecule had sufficient detail and fidelity to allow determination of both temperature and absolute concentration. This occurred for HCN and H_2O in XM39 propellant and for H_2O and CO in JA2 propellant. Dark zone temperatures (1185 K for XM39 and 1433 K for JA2) obtained in this fashion are in good agreement with reported values. All six of the species were found in XM39, and absolute concentration or upper limits are given. No evidence of HCN or N_2O absorption was observed in the dark zone of JA2, thus, four dark zone species concentrations are reported for this propellant. Comparisons of species concentration and dark zone temperature measurements are made with other published measurements under conditions of steady-state, self-sustained propellant combustion.

Introduction

Delayed ignition events that occur in gun firings are thought to be related to detailed chemistry effects of the solid propellant propulsion charge. At moderate pressure ($\sim$2 MPa), where the transition from ignitor burning to the main propellant burning occurs, many solid propellants burn with a clearly observable two-stage flame structure [1]. These two flames are separated by a nonluminous region called the dark zone whose spatial extent is governed by pressure. The length of this dark zone increases with decreasing pressure, and for sufficiently low pressure the second stage "luminous flame" does not form. At high pressures the two stages merge. Overall, these dark zones appear because of the slow conversion of NO to N_2. The chemistry involved in this conversion process is relevant to delayed ignition. Hence, a research effort to supply interior ballistic codes with detailed chemistry for the conversion of the propellant dark zone to the second-stage flame is underway. One of the beginning steps is to probe the dark zone for temperature and species concentration information. This information can be used to develop and test detailed chemical reaction mechanisms.

Absorption spectroscopy with full spectrum least squares data analysis has been developed and used for this purpose. This technique, applied to the UV/visible spectral region, has been used to obtain temperature and NO and OH concentration profiles through the dark zones and luminous flame zones of single-base, double-base, and nitramine propellants [2–6]. Many of the major dark zone species (CO, CO_2, N_2O, H_2O, HCN, CH_4) have no easily accessible transitions in the UV/visible region of the spectrum, thus, absorption spectroscopy in the infrared region has been recently investigated. Two full-spectrum, in situ techniques have been reported: an FTIR method [7] and a multichannel method [8,9]. Here, in addition to experimental improvements, a larger set of species concentrations have been determined by using the HITRAN database [10] as input into a program for data analysis.

Experimental

The absorption experiment and windowed pressure chamber have been described previously [2,3,6,8,9], thus, only pertinent improvements will be discussed here. A sketch of the experiment is shown in Fig. 1. The primary light source was a 250-W quartz-tungsten-halogen lamp. At wavenumbers
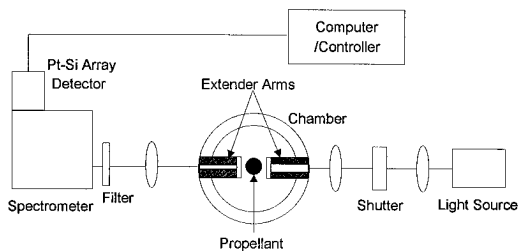
FIG. 1. Sketch of experimental setup. The windowed pressure chamber is shown in cross section to display the minimal chamber path length obtained with added extender arms.

less than 3300 cm^{-1}, a silicon carbide Globar provided greater intensity and was employed for some experiments. CaF_2 lenses directed light through the chamber and focused it onto the entrance slit of a 0.32-m spectrometer containing a 75-groove/mm grating blazed at 2500 cm^{-1}. A liquid nitrogen–cooled focal plane array detector (Princeton Instruments) composed of 1024 platinum-silicide (Pt-Si) elements in a linear configuration was used to detect the dispersed light. When operated in first order, the system has a total spectral window of about 1100 cm^{-1} when centered on 3000 cm^{-1} with a spectral resolution of about 6 cm^{-1} using a 125-μm entrance slit. Spectral calibrations were performed using a low-pressure argon lamp. This array detector is sensitive from about 2250 to 11,000 cm^{-1}, and when used with the Princeton Instruments ST-120 controller, a scan rate of 10 μs/diode (i.e., 10.24 ms is needed to read out the entire diode array) is obtained with a dynamic range of 14 bits.

An IR longpass filter was used between the sample chamber and spectrometer to remove any higher-order light, as well as visible radiation emanating from the burning propellant. Radiation emitted from the flame is more of a problem in the IR region than in the UV region, and a fast shutter with a minimum opening time of 1.8 ms (Vincent Associates Model LS6) was placed between the light source and the chamber. Thus, a spectrum consisting of the background, the dark charge, and any emission from the sample was available for subtraction from the spectrum of the transmitted light. In order to compensate for the finite time required by the shutter to open or close, the frequency of the shutter was set to one-fourth of the frequency of a master clock controlling the readout of the diode array. This allows every other spectrum to be acquired while the shutter is either fully opened or fully closed. The time to acquire one data pair (two spectra) is 42 ms when signal averaging is required, or 32 ms for a single-shot experiment. The ability to acquire both IR absorption and emission spectra sequentially at a fast acquisition rate and with low noise provides advantages over other diagnostic techniques applied to solid propellant flames.

Although the space surrounding the cylindrical propellant sample is purged with flowing nitrogen [3], combustion products may still migrate into this region. Concentrations of these products were minimized by reducing the path length to about 0.4 cm larger than the propellant sample diameter. This was accomplished by extender arms terminated with sapphire windows. When possible, propellant samples with a larger diameter were used (1.08 cm vs. 0.64 cm) to increase the ratio of the sample length to the total path length. The overall spatial resolution of 0.25 cm was set by the inside diameter of the extender arm on the spectrometer side. Spectra obtained in this study were acquired in the dark zone at an average height of 0.15 cm directly above the propellant burning surface.

Data Analysis

The governing equations for absorption have been discussed previously [2,3] and are based on the differential absorption law where $I(v)$, the transmitted intensity of light at frequency v, is attenuated along a path of length l according to

$$I(v) = I_0 \exp\left[-k_v l\right]$$

If a background absorption occurs over the pathlength and is only weakly dependent on v, then

$$I(v) = I_0 B(v) \exp\left[-k_v l\right]$$

where I_0 is the incident light intensity, k_v is the absorption coefficient for the molecule of interest, and $B(v)$ is the baseline correction factor for any broadband attenuation along the path length. For conditions where the light source and spectrometer bandwidths are much larger than the width of the absorption line, an instrument function, $S(v, v_0)$, centered at v_0, is introduced to give

$$I_t = \int S(v, v_0) I(v) dv$$

where I_t is the integrated light transmitted.

A nonlinear, multivariate, least-squares-fitting-program using a Simplex algorithm [11] has been written for use within the Galactic Industries' GRAMS/386 environment. Molecular parameters and transition line strengths needed for the calculation of k_v are obtained from the HITRAN [10,12] database. The linewidths for the instrument function were obtained from a low-pressure argon lamp whose shape was well approximated by a Gaussian function.

The data analysis procedure has been tested previously [13] by fitting experimental spectra obtained from a pressure- and temperature-controlled test cell. These results showed temperature and concentration agreement to 2% and 6%, respectively.