Solid propellant combustion diagnostics using multichannel near infrared absorption spectroscopy

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Introduction

The combustion of solid propellants has been under investigation for many years; however, the detailed chemical and physical processes are still not completely understood. Many solid propellants burn as a two-stage flame with a luminous portion and a non-luminous "dark zone".¹ The length of this dark zone increases with decreasing pressure and for sufficiently low pressures the luminous flame is not formed. Common gun propellants, i.e. single base (nitrocellulose), double base (nitrocellulose–nitroglycerin) and low vulnerability nitramine propellants exhibit dark zones which arise from the slow conversion of NO to N₂. The delayed ignitions which are found to take place in some gun firings are thought to be related to the chemistry occurring in the dark zone.

Over the last six years this laboratory has developed a multichannel optical absorption technique and applied it to the study of gas-phase, steady-state propellant combustion processes. Results for NO and OH have been obtained for double base and nitramine propellants using a multichannel array detector sensitive in the ultraviolet/visible spectral region.^{2,3} More recently an infrared sensitive photodiode array detector has been used to obtain absorption spectra and concentration estimates for HCN, CH_4 , H_2O , CO, N_2O and H_2CO .^{4–7} We report here updated results for CO and N_2O using symmetric stretch overtone absorptions and a least squares fitting technique.

Experimental

The absorption experiment, as well as the windowed pressure vessel used in this study, have been described in detail previously²⁻⁷ and so only a brief outline will be given here. The experiment consists of a multiplexed 1024 element platinum silicide linear array detector (Princeton Instruments), a 0.320 meter grating spectrometer, a 250 W quartz tungsten–halogen source and windowed strand burner, where cylindrical propellant samples are burned cigarette fashion at moderately high pressures (10–15 atm.). The detector is sensitive from about 0.90 to 4.5 μ m with a maximum quantum efficiency of 8% at 1.2 μ m decreasing to 1% at 3.0 μ m and beyond. When used with the Princeton Instruments ST-120 controller, a scan rate of 10 μ s/diode (i.e. 10.24 ms needed to read out the entire diode array) is obtained with a dynamic range of 14 bits. At wavelengths beyond about 3 μ m the quartz envelope of the quartz tungsten halogen lamp limits the exiting radiation. Thus, this lamp was replaced by a silicon carbide globar commonly used as a light source in commercial Fourier transform infrared (FT-IR) units. About a factor of two improvement was realized at the N₂O wavelength of interest, 3.9 μ m.

In order to test the data analysis procedure of least squares fitting absorption spectra using the HITRAN⁸ database, a temperature-controlled, windowed, stainless-steel, sample-cell was incor-

porated into the experiment. Pure gases of N_2O and CO were introduced into the 1 cm pathlength cell and the gas pressure and temperature set to desired values. The absorption spectra obtained could then be least squares fitted and the results compared to the known values. These comparisons are discussed in the data analysis section.

Data analysis

Based on the differential absorption law for a parallel beam of light of frequency v traveling in the +x direction through a medium with absorption k(v),

$$-dI = Ik(v)dx$$

the intensity of the incident beam, I (assumed to be constant), is attenuated along a path of length l according to

$$I(\mathbf{v}) = I_0 \exp[-lk(\mathbf{v})].$$

If a background absorption occurs over the pathlength and is only weakly dependent on v, the transmitted intensity I(v), can be written as

$$I(\mathbf{v}) = I_0 B(\mathbf{v}) \exp[-k_{\rm w} l]$$

where k_w is the absorption coefficient of the molecule of interest and B(v) represents a multiplicative background correction for a broadband attenuation along the path length. For conditions where the light source and spectrograph bandwidths are much larger than the width of a typical absorption line an instrument function, $S(v,v_0)$, centered at v_0 is introduced to give

$$I_t = \int S(\mathbf{v}, \mathbf{v}_0) \ I_t(\mathbf{v}) \ d\mathbf{v}$$

where I_t is the integrated light transmitted.

A non-linear, multivariate, least-squares-fitting-program using a Simplex algorithm⁹ has been written for use within the Galactic Industries' GRAMS/386 environment. Molecular parameters and transition line strengths needed for the calculation of k_w are obtained from the HITRAN^{8,10} database.

A typical test cell transmittance spectrum and fit for CO is shown in Figure 1. For this experiment the temperature and pressure conditions were set to 423 K and 10 atm., respectively. A least squares fit to this data gives a temperature of 419 K and pressure of 9.86 atm. If it is assumed there is no error in the thermocouple and pressure gauge used to measure the temperature and pressure then the least squares fit for temperature and pressure agrees to within 2%.

Likewise, Figure 2 illustrates a transmittance spectrum and fit for N₂O where the test cell conditions are T = 370 K and P = 1.68 atm. Least squares fitting results in a temperature of 375 K and a pressure of 1.88 atm. Here the agreement in temperature is within 2% and the pressure 6%.

The spectral resolution (2.3 nm) required as an input for fitting was obtained from measuring the width of a helium emission line in the appropriate wavelength region. This spectral resolution incorporated into a Gaussian lineshape function was used to convolute the calculated spectrum to best approximate the effects of the instrument response. Additionally, the individual molecular transitions were approximated by a delta function shape since the light source is broad band and the resolution of the spectrometer is much broader than that of the molecular-rotational-transitions. These simplifications allowed for fitting on a PC. Fitting times of a few minutes were common when using a typical 486 cpu.



Figure 1. Transmittance spectrum for the $2v_1$ overtone of CO. The points are the data and the solid line is the least squares fit.



Figure 2. Transmittance spectrum for the $2v_1$ overtone of N_2O . The points are the data and the solid line is the least squares fit.

Results

A transmittance spectrum for the $2v_1$ absorption of CO taken during steady-state combustion conditions of JA2¹¹ is shown in Figure 3. This spectrum was taken in the center section of the dark zone during combustion at 10 atm. nitrogen pressure. The JA2 propellant sample was a 0.64 cm diameter solid cylinder which was burned cigarette fashion and the absorption pathlength was chosen to be the propellant diameter. Maximum spatial resolution for these experiments was 0.25 cm, the diameter of the light beam. For these small absorptions, less than 1%, averaging of spectra was required. Typically, 100 emission corrected spectra were obtained which takes about four seconds. While this spectra gathering is occurring the propellant feed mechanism is feeding the propellant at about the same rate it is being consumed. This process lowers the spatial resolution somewhat and a conservative estimate for the overall resolution is 0.5 cm. Least squares fitting the data results in a temperature of 1476 K and 0.36 mole fraction of CO. Several other experimental runs were made for these conditions and the averages are reported in Table 1 along with other published results. No signals attributable to N₂O absorption could be identified in the dark zone of JA2 burning at 10 atm. pressure.

A nitramine propellant, XM39,¹² was also investigated and the transmittance spectrum is shown in Figure 4. Larger variations in combustion intensity behavior during the course of an experimental run led to poor signals even though the absorption path length was increased by using 1.08 cm diameter cylindrical propellant samples. Least squares fitting of the XM39 data was done using only concentration as a variable. The temperature was fixed at 1150 K, an average value obtained previously from both IR⁵ and UV/visible¹³ absorption work. The least squares fit for the data shown in Figure 4 gives a CO mole fraction of 0.12. Two experimental runs for these conditions gave an average value of 0.13 which is in the Table. An N₂O overtone absorption region



Figure 3. Transmittance spectrum for the $2v_1$ overtone of CO taken in the dark zone of JA2 propellant burning in 10 atm. nitrogen. The points are the data and the solid line is the fit.



Figure 4. Transmittance spectrum for the $2v_1$ overtone of CO taken in the dark zone of XM39 propellant burning in 10 atm. nitrogen. The points are the data and the solid line is the fit.



Figure 5. Transmittance spectrum for the $2v_1$ overtone of N₂O taken in the dark zone of XM39 propellant burning in 10 atm. nitrogen. The points are the data and the solid line the least squares fit.

	A — XM39	B — XM39	C — JA2	\mathbf{D} — DB2 ¹⁶
Molecule	P = 21 atm	P = 10 atm	P = 10 atm	P = 9 atm
	<i>d</i> = 1.25 mm	d = 1.25 mm	<i>d</i> = 1.25 mm	d = 2 mm
СО	0.10	0.13	0.38	0.38
N ₂ O	0.03	0.021	0	0
Т	1200 K	1150 K	1448 K	1500 K

Table 1. Comparison of CO and N_2O mole fractions measured in XM39 and JA2.

A. Mallery and Thynell.¹⁴

B. Present work.

C. Present work.

D. Lengelle et al.15

was identified in the XM39 spectra and the transmittance is plotted in Figure 5. Here again the temperature was fixed at 1150 K and the best fit for N_2O concentration was a mole fraction of 0.018. Again two experiments gave an average of 0.021.

Several factors were considered for inclusion of published results. All the data in Table 1 are for steady-state unassisted combustion conditions. A direct comparison is available for XM39. In the case of JA2, a similar type propellent, DB2, was chosen. Both propellants are homogeneous and the experimental pressures used are almost identical. The agreement for CO concentration is good for both comparisons. Only the dark zone temperature for JA2 was fitted in the present study and the comparison with DB2 is quite good. Our previously determined temperature^{5,13} for the XM39 dark zone is similar to that of Mallery and Thynell.¹⁴ Detectable quantities of N₂O were found in XM39, however, the signal was noisy due to combustion intensity changes and a low detector quantum efficiency. Moreover, it appears that another species is causing some absorptions. The comparisons indicate about a 40 per cent difference and this variation is probably within the other species interference that we observe, the N₂O concentration value given in Table 1, should more appropriately be considered an upper limit. Infrared detection with InSb elements would give higher efficiency in this wavelength region and provide a more accurate determination of N₂O concentration.

From a detailed chemical kinetic modeling standpoint, establishing an accurate value for N_2O is quite important. The gas composition of the propellant dark zone is fuel rich and thus an oxidizer such as N_2O can play a pivotal role in major chemical steps.

Summary

Infrared overtone absorption spectroscopy has been used to determine CO and N_2O concentrations in representative nitramine propellants (XM39) and homogeneous propellants (JA2). When comparing with published work excellent agreement is found for CO concentrations but only a factor of two agreement for N_2O . More work is necessary to obtain a more accurate value for this important molecule.

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- 9. R. W. Daniels, *An Introduction to Numerical Methods and Optimization Techniques*. North Holland Publ., Amsterdam (1978).
- 10. We used an updated HITRAN database for the CO molecule. This database was developed to be able to better represent higher temperature conditions. HITRAN 1992 was used for the N₂O molecule.
- 11. The major ingredients for JA2 propellant are (by weight per cent): nitrocellulose, 58.2%, nitroglycerin, 15.8% and diethyleneglycoldinitrate, 25.2%. The nitration level of the nitrocellulose is 13.04%.
- 12 The major ingredients for XM39 propellant are (by weight per cent): cyclotrimethylene–trinitramine, 76%, cellulose acetate butyrate, 12%, acetyl-triethyl-citrate, 7.6% and nitrocellulose, 4%. The nitration level of the nitrocellulose is 12.6%.
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- 16. The major ingredients for DB2 propellant are (by weight per cent): nitrocellulose, 52% and nitroglycerin, 43%. The nitration level of the nitrocellulose is 11.6%. The reported gas composition was renormalized to include 0.2 mole fraction H₂O.