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Temperatures and Species Concentration in Propellant Dark Zones via Fitting Infrared (IR) Spectral Absorption Data

by J. A. Vanderhoff, S. H. Modiano,
M. W. Teague, and B. E. Homan

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Abstract

In a continuing investigation of the dark zone of double-base and nitramine propellants during self-sustained combustion, least-squares fitting has been developed and updated simulations of infrared (IR) spectral absorption data. Moreover, additional multichannel absorption experiments have been performed using a longer path length afforded by a "triple pass" arrangement of the light beam.

Propellant dark-zone spectra were obtained over the spectral region from 1,600 to 4,400 nm. Within this range, absorptions for HCN, H_2O, N_2O, CO, CO_2, and CH_4 have been detected through the use of a 1,024-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 have been 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. Comparisons of species concentration and dark-zone temperature measurements are made with other published measurements.

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1. INTRODUCTION

Combustion of solid propellants has been studied 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 nonluminous "dark zone" (Kubota 1980). 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 that arise from the formation of NO and subsequent slow conversion to N_2. The delayed ignitions, found to take place in some gun firings, are thought to be related to the chemistry occurring in the dark zone.

Over the last 8 yr, 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 (Vanderhoff 1991; Vanderhoff, Teague, and Kotlar 1992). More recently an IR-sensitive photodiode array detector has been used to obtain absorption spectra that produce concentration estimates for HCN, CH_4, H_2O, CO, and N_2O (Modiano and Vanderhoff 1993, 1994a, 1994b, 1995, and to be published; Vanderhoff et al. 1996). We report, here, updated results for HCN, H_2O, CO_2, CO, N_2O, and CH_4 using a least-squares-fitting technique.

2. EXPERIMENTAL

The absorption experiment, as well as the windowed pressure vessel used in this study, has been described in detail previously (Vanderhoff 1991; Vanderhoff, Teague, and Kotlar 1992; Modiano and Vanderhoff 1993, 1994a, 1994b, 1995; Vanderhoff et al. 1996). Only pertinent features or changes to the experiment will be described here. One improvement that is very useful is the rate of data collection. Absorption spectra were collected at a repetition rate of approximately 25 Hz. During any 40-ms period, one spectrum is taken with the light passing through the sample region (shutter open) and one taken with the beam blocked (shutter closed). The platinum-silicide array detector has sensitivity over the wavelength range from 900 to 4,400 nm; however, the quartz envelope of the quartz-tungsten-halogen lamp filters radiation at wavelengths beyond ~3,000 nm. Thus, for measurements from 3,000 to 4,400 nm, this lamp was replaced by a silicon carbide Globar (a commonly used light source in commercial Fourier transform infrared [FTIR] instruments) fitted with an ordinary flashlight reflector. About a factor-of-2 increase in light intensity was realized over this wavelength range.

Windows for passage of light through the combustion chamber are mounted at the end of metal extender tubes for close positioning to the propellant sample, thus minimizing the path length inside the chamber, but outside of the combustion region. A modification of this arrangement involved mounting the entrance and exit chamber windows at a slight angle to the beam normal and mirroring a portion of them to produce multiple passes through the sample area, increasing the absorption path length. The triple-pass experimental setup is shown in Figure 1. This setup consists of extenders into the chamber with rectangular apertures and partially gold-coated sapphire windows set at an angle to the centerline. The effective path length, l, can be calculated as

$$l = D + (4 \times X) = D + [4 \times \{(D/2)^2 - h^2\}^{1/2}]$$

or

$$l = 10.8 \text{ mm} + [4 \times \{5.4^2 - 2.7^2\}^{1/2}] = 29.31 \text{ mm},$$

when the diameter of the cylindrical propellant sample is 10.8 mm. This path-length technique was used when measuring the extremely small absorptions encountered for the CO and N_2O overtones. As a point of reference, dark zone lengths studied here were ~1 cm, and the spatial resolution of the experiment 0.25 cm.

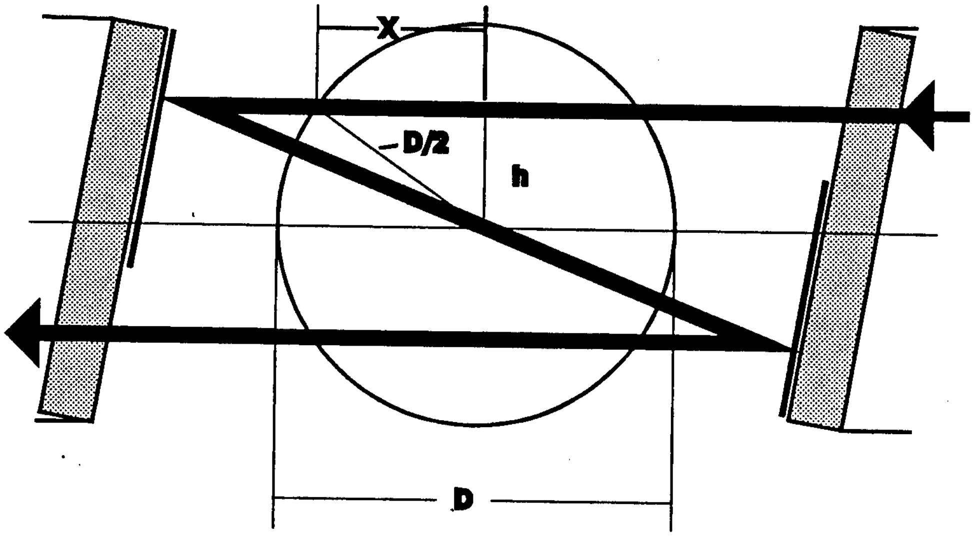

Figure 1. Diagram of triple-pass beam.

In order to test the data analysis procedure of least-squares-fitting absorption spectra using the HITRAN database (Rothman et al. 1992),* a temperature-controlled, windowed, stainless steel sample cell was incorporated into the experiment. Pure gases of N_2O and CO were introduced into the 1-cm path-length cell, and the gas pressure and temperature were set to desired values. The absorption spectra obtained were then least-squares-fitted, and the results were compared to the known values. These comparisons are discussed in section 3.

3. DATA ANALYSIS

The change in intensity of a parallel beam of light with frequency ν traveling through a medium in the +x direction with an absorptivity k(ν), is given by the differential absorption law,

$$dI/I = k(\nu)dx.$$

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* We used an updated HITRAN database for the CO molecule. This database was developed to be able to better represent higher temperature conditions. HITRAN 92 was used for the other molecules.

By integrating along the path length l, the intensity, after having traversed the region of interest, is given by

$$I = I_o \exp[-k(\nu) l].$$

If a background absorption occurs over the path length and is only weakly dependent on ν, the transmitted intensity $I(\nu)$, can be written as

$$I(\nu) = I_o B(\nu) \exp[-k_w l],$$

where k_w is the absorption coefficient of the molecular transition of interest, and $B(\nu)$ represents a multiplicative background correction for a broad-band 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, $S(\nu,\nu_o)$, centered at ν_o is introduced to give

$$I_t = \int S(\nu,\nu_o) I(\nu) d\nu,$$

where I_t is the integrated light transmitted.

A nonlinear, multivariate, least-squares-fitting program using a Simplex algorithm (Daniels 1978) 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 database (Rothman et al. 1992). In all cases, the exponential form of the absorption law was used.

To test the fitting program, a static test was employed. A typical test-cell transmittance spectrum and fit for CO are shown in Figure 2. For this experiment, the temperature and pressure conditions were set to 423 K and 1.033 MPa, respectively. A least-squares fit to these data gives a temperature of 419 K and a pressure of 1.018 MPa. If it is assumed that there is no

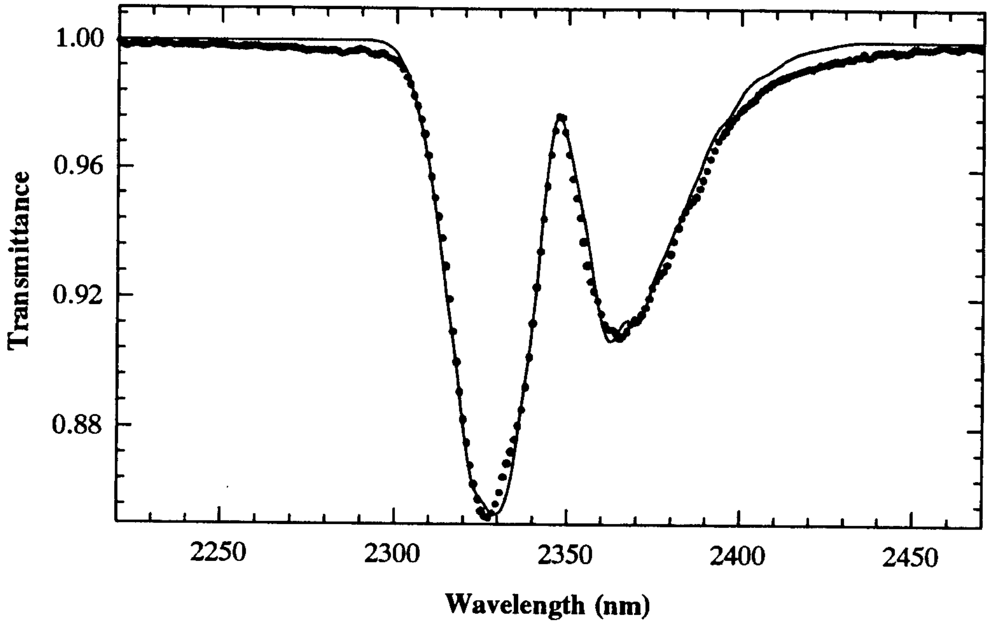

Figure 2. Absorption spectrum for the $2\nu_1$ overtone of CO in a static cell at 423 K and 1.033 MPa. The points are the data, and the solid line is the least-squares fit.

error in the thermocouple and pressure-gauge measurements, then the least-squares fit for temperature and pressure agrees to within 2%.

Likewise, Figure 3 illustrates a transmittance spectrum and fit for N_2O, where the test-cell conditions are T = 370 K and P = 0.174 MPa. Least-squares-fitting results in a temperature of 375 K and a pressure of 0.194 MPa. Here, the agreement in temperature is within 2% and the pressure 6%. For N_2O, the database does not include all involved transitions as evidenced by the abrupt change to 100 % transmission around 3,975 nm.

The line width (2.3 nm, half width at half maximum) required as an input for fitting was obtained by measuring the width of an argon emission line in the appropriate wavelength region. This emission line, well fit by a Gaussian line-shape function, was thus 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

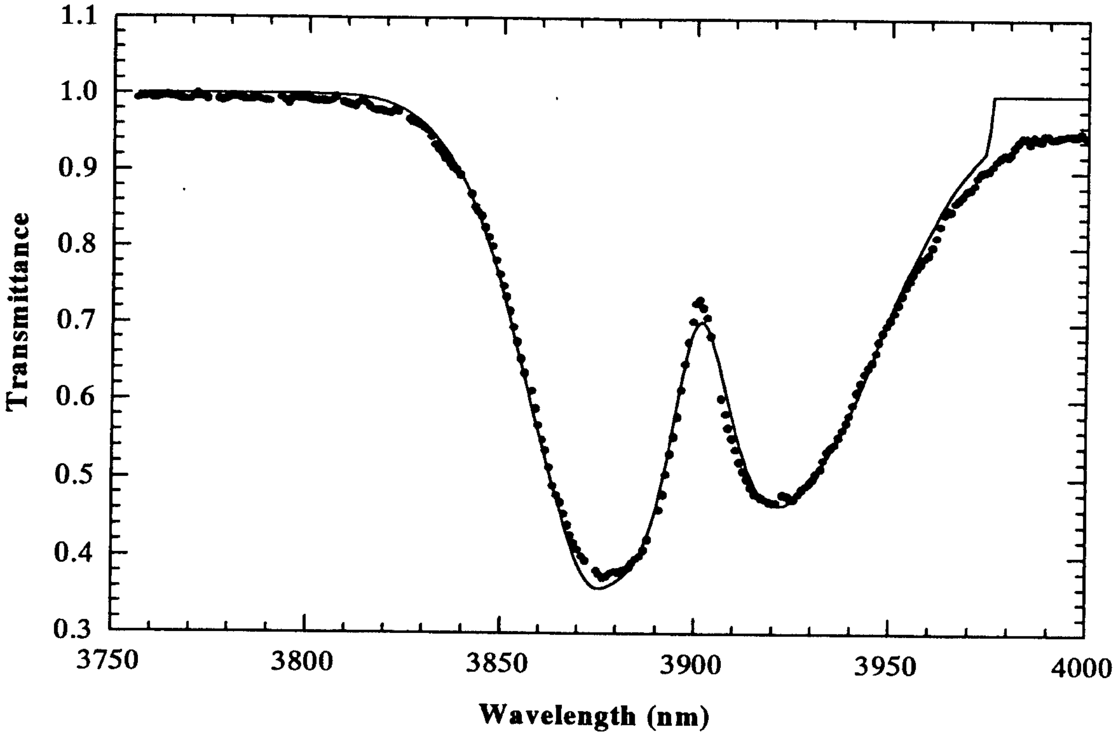

Figure 3. Absorption spectrum for the $2\nu_1$ overtone of N_2O in a static cell at 370 K and 0.174 MPa. The points are the data, and the solid line is the least-squares fit.

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.

4. RESULTS

The transmission spectra of XM39* and JA2† propellants taken in the dark-zone region during steady-state combustion conditions in 1-MPa nitrogen are shown in Figure 4. Six species,

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* The major ingredients for XM39 propellant are (by weight-percent) 76% cyclotrimethylene-trinitramine, 12% cellulose acetate butyrate, 7.6% acetyl-triethyl-citrate, and 4% nitrocellulose. The nitration level of the nitrocellulose is 12.6%.

† The major ingredients for JA2 propellant are (by weight-percent) 58.2% nitrocellulose, 15.8% nitroglycerin, and 25.2% diethyleneglycoldinitrate. The nitration level of the nitrocellulose is 13.4%.

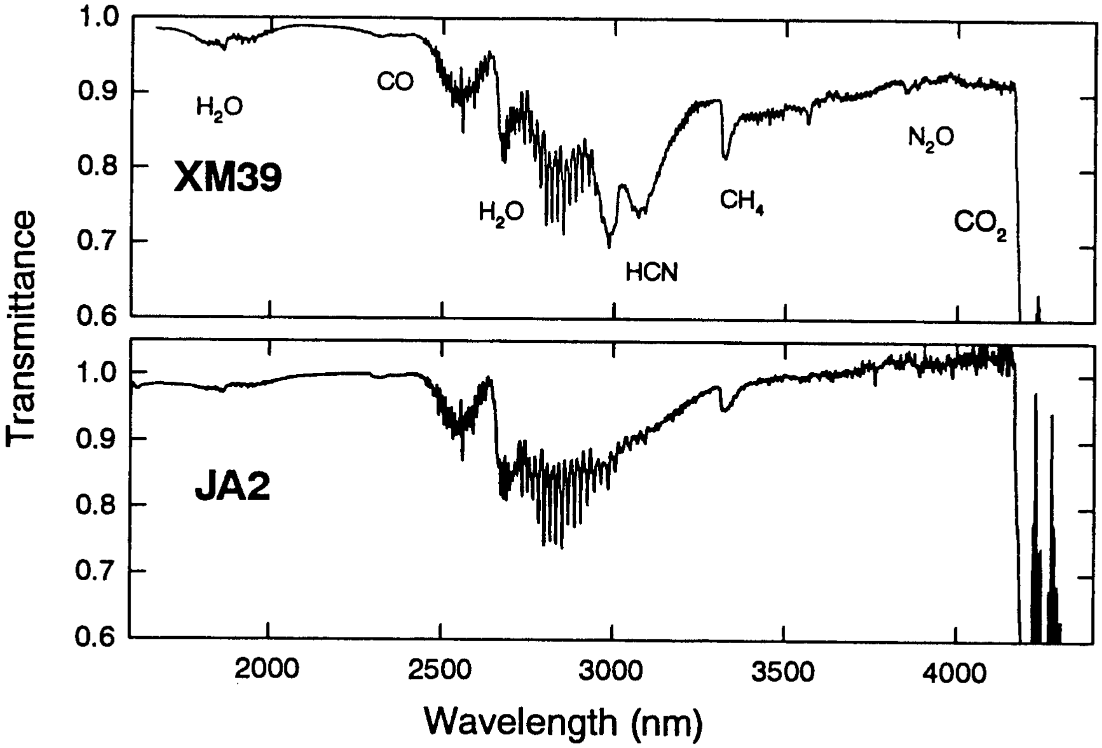

Figure 4. Dark-zone absorption spectra for XM39 and JA2 propellants under self-sustained combustion conditions in 1.0-MPa nitrogen. These IR absorption spectra were taken at an average distance of 0.15 cm from the propellant surface.

labeled on the XM39 spectrum, have been identified as exhibiting absorption over this region. Prominent absorptions for H_2O are found in the 2,400- to 3,100-nm region and can be assigned to the ν_1 (2,734 nm) and ν_3 (2,662 nm) fundamental vibrational bands. A combination band, $\nu_2 + \nu_3$ (1,875 nm) for H_2O has smaller absorption features in the 1,700- to 2,000-nm region. The largest absorption observed starts around 4,250 nm and is the asymmetric stretch of CO_2. Other readily identifiable absorption features are the fundamental CH stretch of CH_4 at 3,311 nm and the fundamental CH asymmetric stretch of HCN at 3,020 nm. Two overtone bands at 2,330 and 3,900 nm are identified as CO and N_2O, respectively. When comparing the spectra of XM39 with JA2, the absence of HCN in the JA2 spectrum is apparent. Looking in more detail, there is no identifiable N_2O absorption for JA2, and the broader shape of the CH_4 absorption indicates the JA2 spectrum is hotter. Each of these features for the six species has been examined more closely by least-squares-fitting to extract temperature and concentration information.

Least-squares fits of H_2O structure in the fundamental band regions for XM39 and JA2 propellants burning in 1-MPa nitrogen are shown on Figures 5 and 6, respectively. Fits are represented by solid or dashed lines, while the data are represented by points. For Figure 5, both the symmetric and asymmetric stretches are fitted. For Figure 6, only the asymmetric stretch region is fitted. Results of fitting the H_2O combination band for the case of XM39 are shown in Figure 7. The amount of absorption and, thus, the signal-to-noise is greater for the fundamental absorptions shown in Figures 5 and 6. Two different experiments (propellant burns) were required to obtain the data of Figures 5 and 7. In addition, another pair of experiments was performed for both XM39 and JA2. The temperatures and H_2O concentrations obtained from these experiments are averaged, and these values are reported in Table 1. In all cases, averaged values are reported in Table 1 and, thus, may differ slightly from the fitted value given in the figure caption. These spectra indicate higher dark-zone temperatures and H_2O concentrations for JA2. Analyses of two different H_2O spectral absorptions (Figures 5 and 7) give identical temperature, but differing concentrations. Uncertainty in the exact shape of the baseline contributes to this variation.

Figures 8 and 9 illustrate fundamental absorptions for CO_2 in the combustion of JA2 and XM39, respectively. This is the end of the sensitivity range for the Pt-Si array detector, and when combined with the absence of detailed features, significant uncertainty arises when fitting for both concentration and temperature. Consequently, the temperatures were fixed, and the only fitting variable was concentration.

A substantial absorption for HCN is observed in the dark zone of XM39, and Figure 10 displays the data (points) and a least-squares fit (solid line) for steady-state combustion at 1.0-MPa nitrogen pressure. The fit to the data deviates the most around 3,020 nm, showing a much more pronounced separation of the P and R branches. Additionally, significant deviation appears in the 3,125- to 3,225-nm region. Recently, it has been reported (Mallory and Thynell 1995) that significant amounts (3 to 4 %) of C_2H_2 are present in the dark zone of this propellant flame. Acetylene does have absorption features in this wavelength range, so C_2H_2 contributions

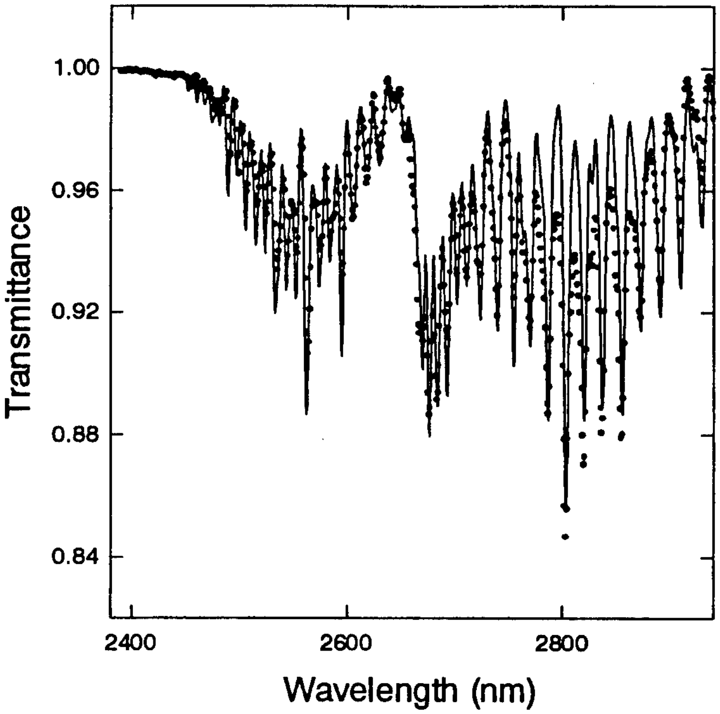

Figure 5. Absorption spectrum of H_2O taken in the dark zone of XM39 burning in 1.0-MPa nitrogen. A best fit for temperature and concentration are 1,204 K and 0.12 mole fraction, respectively.

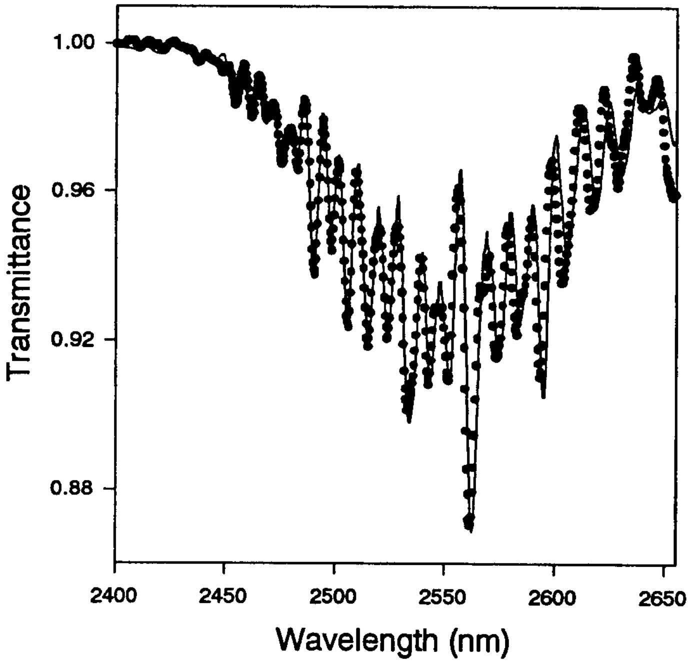

Figure 6. Absorption spectrum of H_2O taken in the dark zone of JA2 burning in 1.0-MPa nitrogen. A best fit for temperature and concentration are 1,402 K and 0.22 mole fraction, respectively.

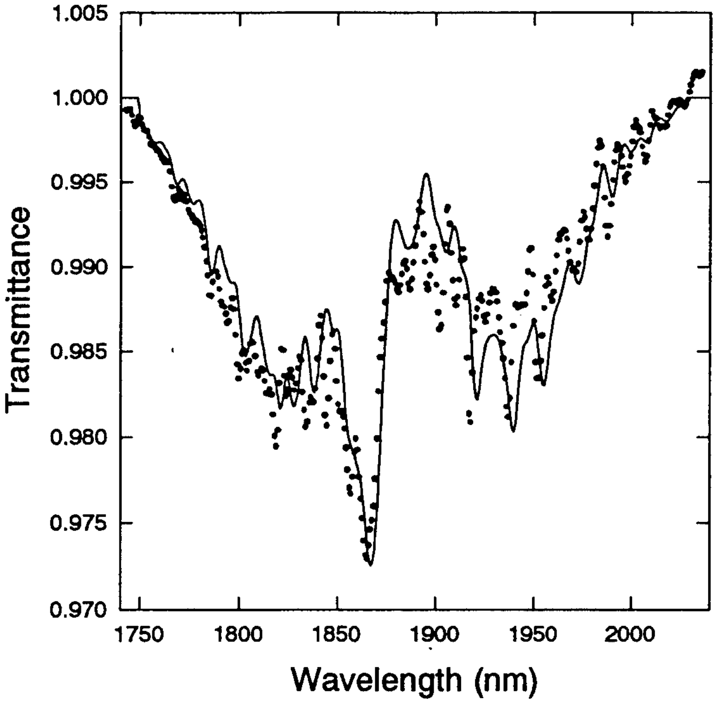

Figure 7. Absorption spectrum of the $\nu_2 + \nu_3$ combination band of H_2O. Spectrum taken in the dark zone of XM39 burning in 1.0-MPa nitrogen. Best fit gives a temperature of 1,204 K and 0.17 mole fraction.

Table 1. Comparison of Dark-Zone Temperatures and Species Concentrations for Double-Base (JA2) and Nitramine-Based (XM39) Solid Propellants.

Species	A - XM 39	B - XM 39		C - JA2	D - JA2	
	(mole fraction)	(Temp. K)	(mole Fraction)	(mole fraction)	(Temp - K)	(mole fraction)
CO	<0.15	1,040	0.12	0.26	1,448	0.38
H_2O	0.05	1,204	0.15	0.08	1,418	0.23
CO_2	NQ	T1	0.04	NQ	T2	0.11
N_2O	<0.07	T1	≤0.018	NO	NO	NO
HCN	0.18	1,153	0.13	NO	NO	NO
CH_4	0.015	1,011	0.007	0.01	1,196	0.014

The prior data analysis (Modiano and Vanderhoff 1995) used spectral simulation (columns A and C), and the results presented here (columns B and D) are derived from least-squares-fitting of the individual absorption spectra. All results in Table 1 are for a nitrogen pressure close to 1.0 MPa.

NQ - Not quantified.

NO - Not observed.

Notes: T1 - Temperature set to 1,150 K.

T2 - Temperature set to 1,450 K.

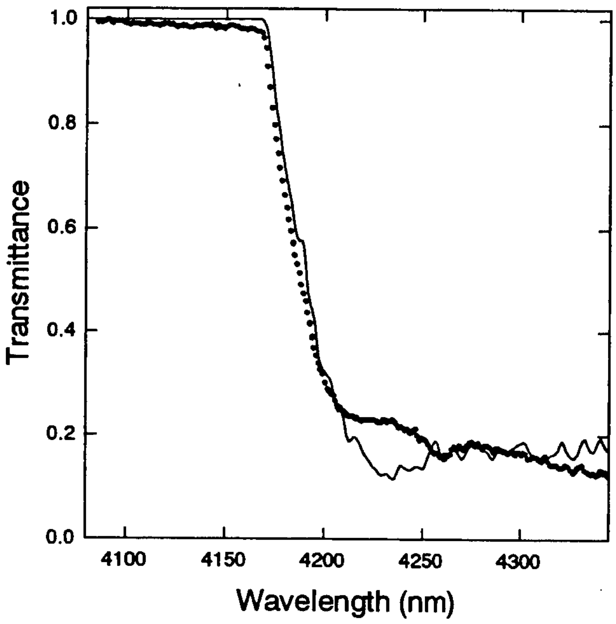

Figure 8. Absorption spectrum of CO_2 taken in the dark zone of JA2 burning in 1.0-MPa nitrogen. The temperature is fixed at 1,400 K, and the best fit for CO_2 concentration is 0.10 mole fraction.

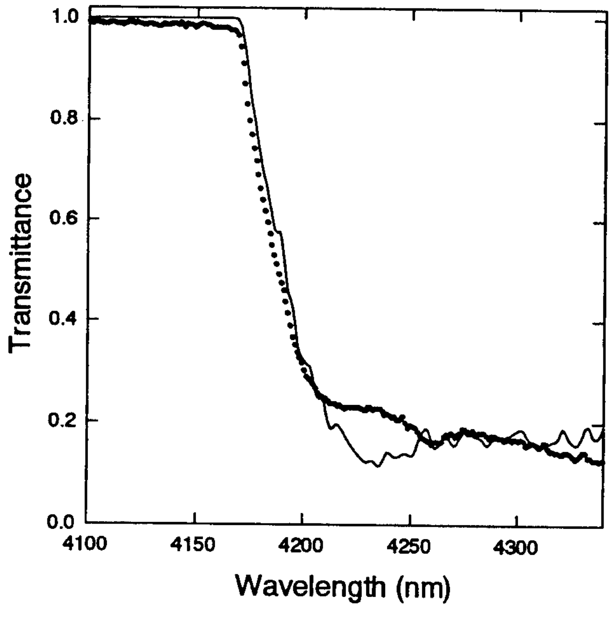

Figure 9. Absorption spectrum of the ν_3 stretch of CO_2. Spectrum taken in the dark zone of XM39 burning in 1.0-MPa nitrogen. The temperature was held fixed at 1,150 K, and the best fit gives a 0.04 mole fraction CO_2.

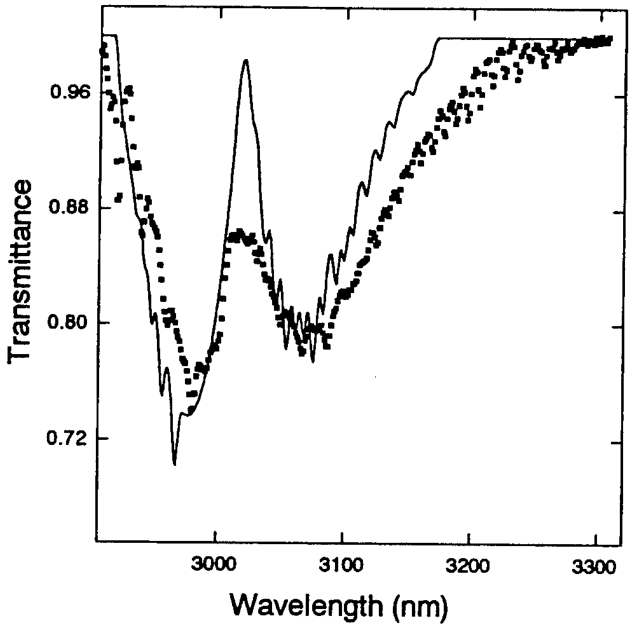

Figure 10. Absorption spectrum of HCN taken in the dark zone of XM39 burning in 1.0 MPa nitrogen. A best fit for temperature and concentration are 1,173 K and 0.14 mole fraction, respectively.

could be present in the data shown on Figure 10 and/or the HITRAN database for HCN is not accounting for all of the high-temperature effects. Evidence suggesting that the absorption features displayed on Figure 10 are predominantly HCN is concluded from the results shown on Figure 11. The data of Figure 11 come from the transmittance obtained after the XM39 propellant has been consumed, but prior to the chamber being completely purged by the flowing nitrogen gas. Both HCN and C_2H_2 should remain in the gas phase at close-to-room-temperature while gas-phase H_2O absorptions disappear because of condensation. A least-squares fit to the data of Figure 11, assuming the species is HCN, is shown as a solid line. The dashed line represents a fit, assuming the species is C_2H_2. Clearly, the HCN fit follows the experimental data much more closely and gives a quite reasonable value of 314 K for temperature. A meaningful concentration value is not available since, in this case, the path between the chamber windows is occupied with a nonuniform mixture of gases.

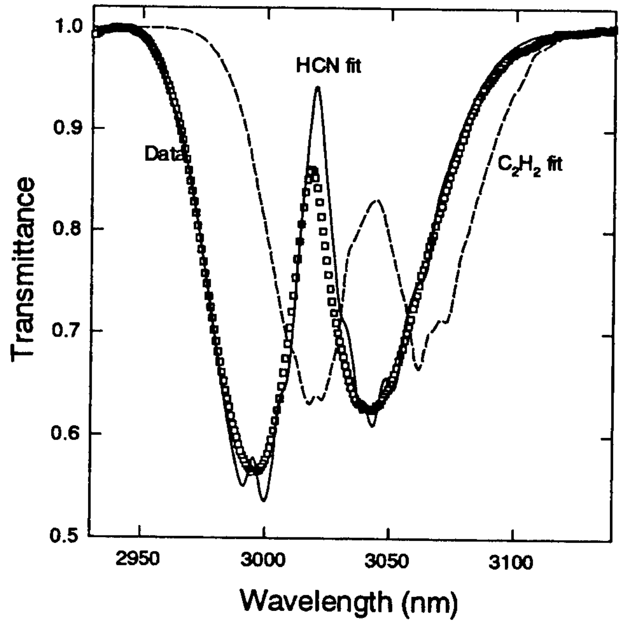

Figure 11. Absorption spectrum in the region of the ν_3 stretch of HCN. Spectrum obtained after flame extinguishment of XM39 propellant. The open squares are the data, the solid line a least-squares fit, assuming the species is HCN and the dashed line, assuming the species is C_2H_2. Assuming the spectrum is HCN, the fitted temperature is 314 K.

Distinct absorption features associated with CH_4 were present in the dark zones of both XM39 and JA2 propellants. The fundamental CH stretch for CH_4 occurs in the 3,311-nm region, and three absorption spectra covering this region are shown on Figures 12–14. A CH_4 absorption spectrum taken after XM39 flame extinguishment (same conditions as for Figure 11) is shown on Figure 12. A good fit to the data is observed for the R and Q branches, while, for the P branch, there is a broad underlying feature not accounted for by the fit. The best fit for temperature is low. Assuming that the temperature is 314 K (determined from the results of Figure 11), then the error here is 12%. Absorption spectra for CH_4 in the dark zones of XM39 and JA2 are displayed in Figures 13 and 14, respectively. Here, there is a much more pronounced deviation between the data and the fits in the 3,350- to 3,400-nm region. It appears that, at higher temperature, the CH_4 Q-branch is not being adequately represented by the database. In both cases, the fitted temperatures are low. If one assumes, however, that the 12% error can be applied at this higher

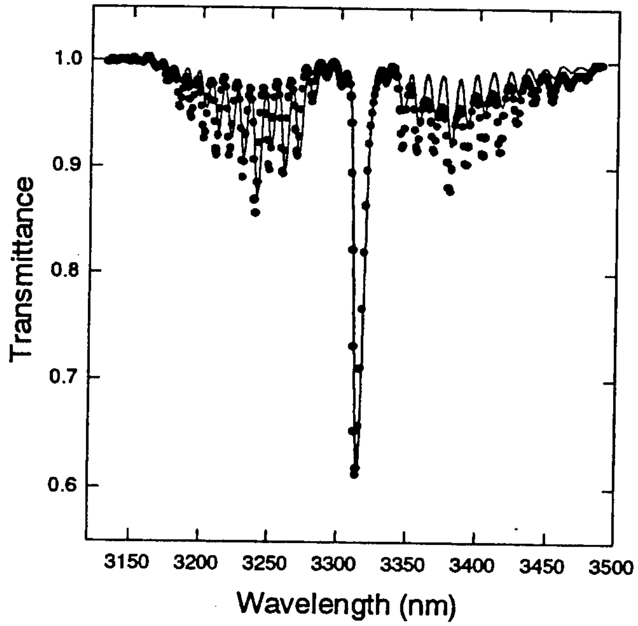

Figure 12. Absorption spectrum of CH_4 obtained after flame extinguishment of XM39 propellant. The best fit for temperature is 276 K.

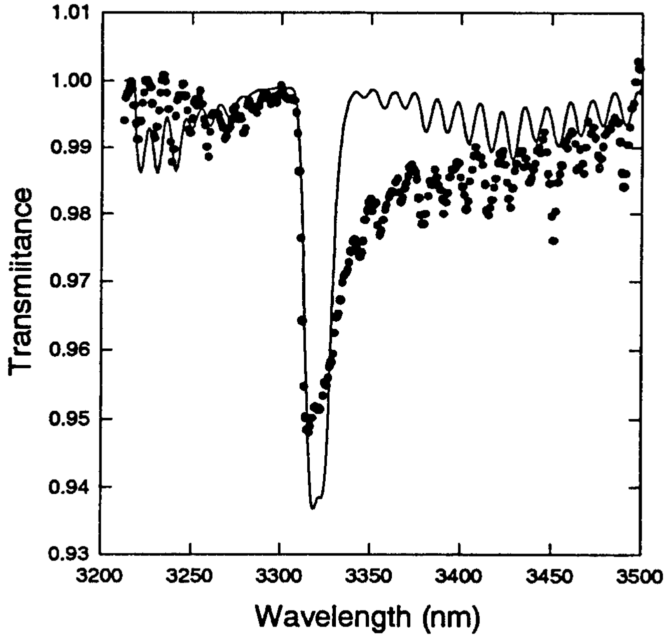

Figure 13. Absorption spectra of the fundamental stretch of CH_4 taken in the dark zone of XM39 burning in 1.0-MPa nitrogen. A best fit yields a temperature of 1,011 K and a 0.007 mole fraction.

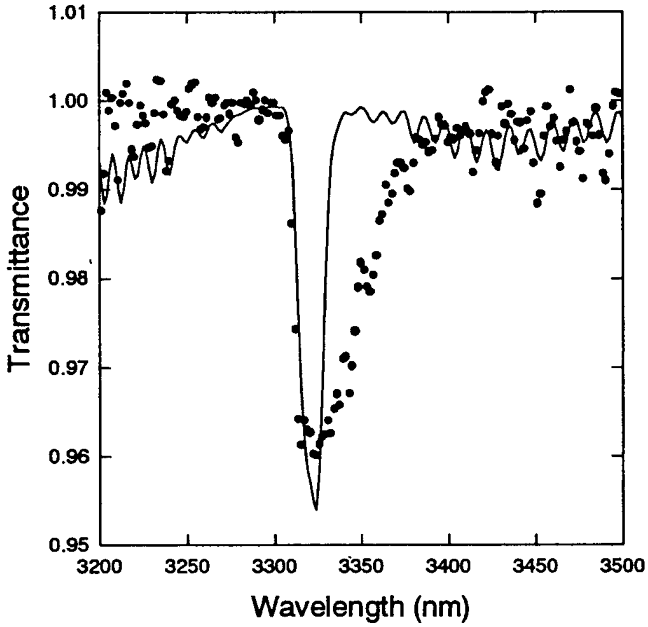

Figure 14. Absorption spectra for CH_4 taken in the dark zone of JA2 burning in 1.0-MPa nitrogen. A best fit yields a temperature of 1,196 K and a 0.014 mole fraction.

temperature situation, then the fitted temperatures are in reasonable agreement with other results reported here and elsewhere (Vanderhoff, Teague, and Kotlar 1992; Teague, Singh, and Vanderhoff 1993).

A recent article by Nagali et al. (1996) indicated that the HITRAN 92 partition function for CH_4 was incorrect at the higher temperatures. When compared to a simple harmonic oscillator (SHO) model (see Herzberg 1960), it was about 40% low at 1,000 K. Consequently, the CH_4 partition function was computed via the SHO model over the range from 500 to 1,500 K. These partition-function values were then fitted to a cubic equation—a form whose coefficients are accepted by the HITRAN 92 database. The derived coefficients are $a = -1.647 \times 10^4$, $b = 6.893 \times 10^1$, $c = -9.107 \times 10^{-2}$, and $d = 4.638 \times 10^{-5}$ and were used in fitting the high- temperature CH_4 absorption spectra shown in Figures 13 and 14.

In addition to fundamental and combination band absorptions, small overtone absorptions were observed for CO and N_2O. A triple pass arrangement (Figure 1) was incorporated to enhance these absorptions, and resultant absorption for CO in JA2 and XM39 are shown in Figures 15 and 16, respectively. N_2O absorption signals were observed in the dark zone of XM39, but not JA2. The results for XM39 are plotted in Figure 17, where the fit to the data does not well represent the finer structure. The fitting program was not stable when both temperature and concentration were allowed to vary. The fit shown in Figure 17 was obtained by fixing the temperature at 1,150 K. Considering the inability to account for the structural detail, which could result from another molecular species participating in the absorption, the best fit of 0.018 for the N_2O mole fraction should be taken as an upper limit.

5. DISCUSSION

In the last section, an abundance of dark-zone absorption spectra was presented. The results of the least-squares fits for temperature and concentration are tabulated in this section and compared with each other, as well as other literature sources. Table 1 contains present data from section 4, as well as previously published data from this laboratory. Data for both nitramine (XM39) and double-base (JA2) propellants undergoing self-sustained combustion in 1.0-MPa nitrogen are presented here. In the spectral simulation data, columns A and C, the temperature for the dark zone of XM39 was fixed to a value of 1,150 K as determined from a band-spread analysis of HCN (Modiano and Vanderhoff 1995) and from fitting NO absorption spectra (Teague, Singh, and Vanderhoff 1993) and 1,450 K for JA2 also from fitting NO absorption spectra (Vanderhoff, Teague, and Kotlar 1992). Shown in columns B and D are temperatures obtained from least-squares-fitting for individual molecules. For the XM39 case, H_2O and HCN provide the most spectral detail and excellent signals and, thus, should provide the best measure of temperature. Within experimental uncertainty, both agree with a value of 1,150 K, as determined previously. Temperatures for XM39 obtained from fitting CO or CH_4, are lower. The CH_4 fit is a poor representation of the data. Moreover, while the close-to-room-temperature fit for CH_4 looks much better, the temperature fit here is also about 10% low. For the JA2 case, good agreement with a prior established value of 1,450 K comes from spectral fits of H_2O and

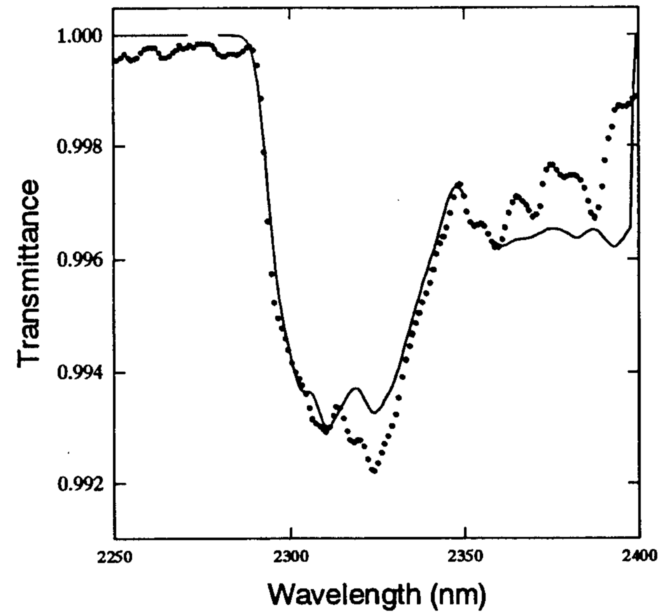

Figure 15. Overtone absorption spectrum of CO taken in the dark zone of JA2 burning in 1.03-MPa nitrogen. Single-pass arrangement. A best fit yields a temperature of 1,476 K and a 0.36 mole fraction CO.

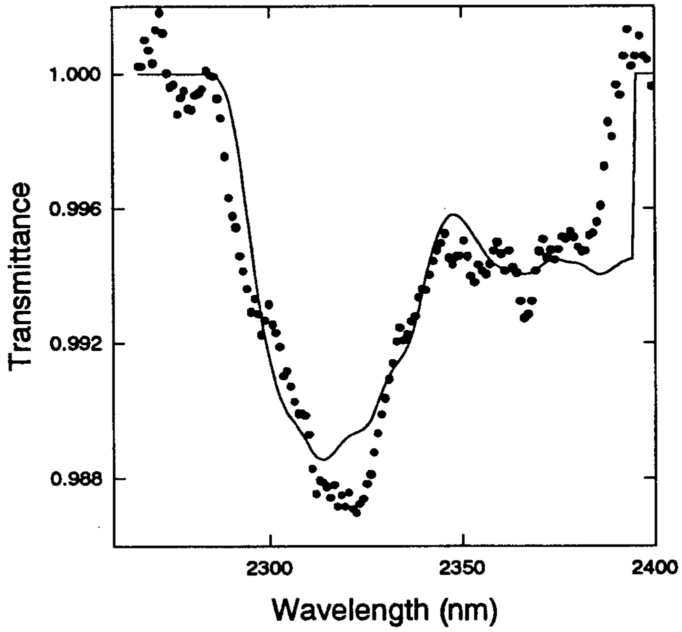

Figure 16. Overtone absorption spectrum of CO taken in the dark zone of XM39 burning in 1.25-MPa nitrogen. Triple-pass arrangement. A best fit yields a temperature of 1,040 K and a 0.10 mole fraction CO.

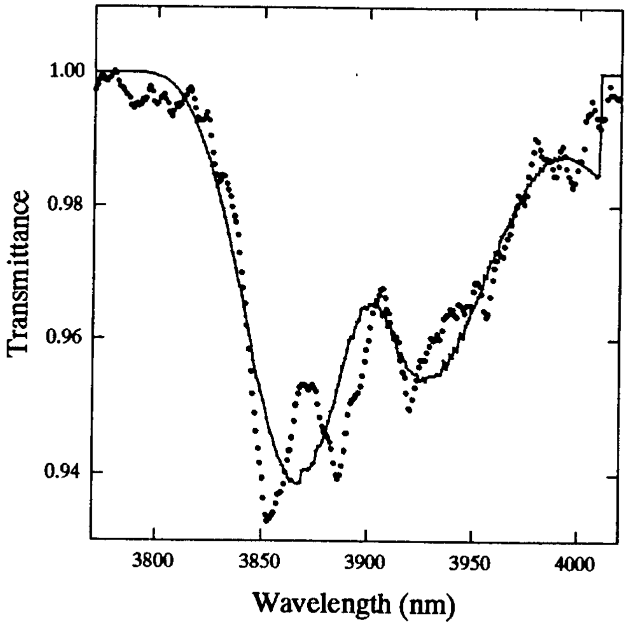

Figure 17. Absorption spectrum for the $2\nu_1$ overtone of N_2O taken in the dark zone of XM39 propellant burning in 1.25-MPa nitrogen using triple-pass optics. Fixing the temperature to 1,150 K, a best fit to the data yields a 0.018 mole fraction for N_2O.

CO. Species concentrations have changed substantially due to the results of the spectral-fitting analysis. The biggest changes have been to almost triple the concentration of H_2O and are supported by fits of both the fundamental (Figure 5) and combination (Figure 7) bands. Concentrations for CO_2 have been determined. Improved values, or upper limits, for the remaining listed molecules are reported.

An important process in experimental data analysis is comparison with other work. However, in many cases exact comparisons are not possible. For the case at hand, some of the most common differences are different samples, laser-assisted vs. self-sustained combustion, and different pressure regimes. Table 2 compares the present data to other published work. The propellant and pressures studied are listed in the Table. It should also be pointed out that the

Table 2. Comparison of the Present Data With Published Dark-Zone Temperatures and Species Concentrations for XM39 and JA2 Propellants.

Species	B-XM39	E-XM39	F-XM39	D-JA2	G-JA2	H-DB2
P (MPa)	1.0	2.2	0.1	1.0	0.1	0.9
Ht (cm)	0.15	0.05	0.5	0.15	0.2	0.2
T_{DZ} (K)	1150	950	1130	1450	1890	1500
CO	0.12	0.09	0.08	0.38	<0.36	0.38
H_2O	0.15	0.09	0.21	0.23	0.14	0.20
CO_2	0.04	0.04	0.05	0.11	0.10	0.085
N_2O	≤0.018	0.02	0.03	NO	NQ	NO
HCN	0.13	0.04	0.21	NO	NQ	NO
CH_4	0.007	0.005	0.01	0.014	NQ	0.026

Notes: The last column shows data for a double base propellant (DB2) similar to JA2 in that the energy content is about the same.
E-XM39 - Mallory and Thynell (1995).
F-XM39 - Tang, Lee, and Litzinger (1994); Fetherolf et al. (1991); and Kuo et al. (1995).
G-JA2 - Liiva, Fetherolf, and Litzinger (1991).
H-DB2 - Lengelle et al. (1984). (The double-base propellant (DB2) by weight-percent consists of 52% nitrocellulose (11.6% nitration), 43% nitroglycerin, and 3% ethyl centralite.)
Ht - Distance above combusting propellant surface where species and temperature measurements were obtained.
NO - Not observed.
NQ - Not quantified.

results of columns F and G were obtained under laser-assisted combustion conditions. All other results reported are for self-sustained combustion. Given these caveats, comparisons are now discussed. There is a two-out-of-three agreement for the dark-zone temperature of XM39. Ulas et al. (1995) use NO absorption spectroscopy measure temperatures around 1,150 K for the dark zone of XM39 when burning in a 1.69-MPa nitrogen environment. Two out of three temperatures are also in agreement for double-base-like propellants. Additionally, Heller and Gordon (1955) measure a dark-zone temperature of 1,600 K for a more energetic double-base propellant. The species concentrations are in reasonable accord for the double-base propellant with CH_4 and H_2O exhibiting the largest differences. Our fitting analysis of the CH_4 absorption spectra contains large (factor-of-2-type) uncertainties in the concentration. The largest excursions in the species concentrations for the dark zone of XM39 are for the HCN and N_2O species. For HCN, we are between the measurements of Mallory and Thynell (1995) and Tang et al. (1994). Mallory and Thynell (1995) attribute their FTIR spectral absorption feature to contributions from both HCN and C_2H_2. We have evidence indicating that this absorption feature is only due to HCN.

N_2O is a reactive oxidizer and, given that the propellant dark zone is fuel-rich, can play a pivotal role in the major chemical steps determining the overall kinetics. We have interpreted our measurements to be an upper limit to the amount of N_2O in the dark zone of XM39, and this upper limit is lower than the other reported measurements. It can be argued that, in the case of the lower pressure, laser-assisted work of Tang, Lee, and Litzinger (1994), the reaction zones are extended due to less collisional chemistry. Hence, reactive species, such as N_2O, extend into the dark zone. Additional support for this position comes from noting that another reactive species, CH_2O, is also present at about the 5% level, and both CH_2O and N_2O are observed to decrease in concentration with increasing distance from the propellant surface. The N_2O mole fraction of 0.02 obtained by Mallory and Thynell (1995) is slightly higher than our stated upper limit. However, this value contains considerable uncertainty (i.e., for their selected N_2O spectral region of analysis, contributions from overlapping of the P-branch of CO_2 and the R-branch of CO are present.

6. SUMMARY

Improvements in the IR absorption spectroscopy experiment at the U.S. Army Research Laboratory have permitted better measurement and analysis of the dark-zone temperature and combustion species (H_2O, HCN, CO, CO_2, and N_2O) concentrations in double-base and nitramine-type propellants. In addition to an in situ multipass arrangement for increasing path length and, thus, absorption signal, the information contained in the multifeatured absorption spectra has been put to use by a least-squares-fitting process. Here, quantitative temperatures and species concentrations are obtained through exclusive use of basic spectroscopic information. No calibration factors are required.

Considering the experimental uncertainties and differing experimental parameters, there exists good agreement among the data sets for the dark zone of double-base propellants. The nitramine propellant studied here (XM39) does not burn well at low pressure (a design feature to make these propellants less vulnerable to unplanned ignition stimuli). Thus, these measurements exhibit more scatter. Potentially, the single most important dark-zone species is the reactive oxidizer N_2O. To determine a more accurate concentration for this moiety, IR detection with InSb elements would give higher efficiency in the overtone wavelength region, as well as provide sensitivity in the fundamental absorption region.

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In a continuing investigation of the dark zone of double-base and nitramine propellants during self-sustained combustion, least-squares fitting has been developed and updated simulations of infrared (IR) spectral absorption data. Moreover, additional multichannel absorption experiments have been performed using a longer path length afforded by a "triple pass" arrangement of the light beam.

Propellant dark-zone spectra were obtained over the spectral region from 1,600 to 4,400 nm. Within this range, absorptions for HCN, H_2O, N_2O, CO, CO_2, and CH_4 have been detected through the use of a 1,024-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 have been 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. Comparisons of species concentration and dark-zone temperature measurements are made with other published measurements.

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