

MEASUREMENT OF THE COMBUSTION TEMPERATURE OF A SOLID PROPELLANT BY THE CARS METHOD

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To measure the solid-propellant combustion temperature, a procedure was used based on examination of the temperature dependence of the Q-branch of the coherent anti-Stokes Raman scattering (CARS) spectrum due to nitrogen contained in combustion products. The measurements were carried out at a pressure of 4 MPa, under which the spectrum demonstrated a substantial overlap between spectral lines. CARS intensities at two frequencies were registered; their ratio was used to determine the combustion temperature of a stoichiometric ammonium dinitramide–polycaprolacton mixture.

The combustion in solid rocket motors proceeds at a pressure of 4–8 MPa and a temperature of 2500–3200 K. The chemical-reaction zone, located in a close vicinity of the burning surface, follows the latter with a velocity of 10–40 mm/sec. Chemically aggressive substances and solid particles contained in the flow of gaseous reaction products hamper the determination of flow parameters, the flame temperature being the most important one. Under such conditions, the use of optical methods such as coherent anti-Stokes Raman spectroscopy, distinguished for their fast response and high spatial resolution and simultaneously not introducing any gas-dynamic disturbances into the burning zone, is most preferable. The CARS method implies the use of an experimental facility for exciting and registering scattered radiation and spectral-data processing tools, which include codes for computing the spectra of tested molecules at elevated temperatures and pressures. In the CARS procedure, two laser-emitted photons with a fixed frequency ω_1 and one photon with a Stokes frequency ω_2 interact with a molecule of a definite type, for instance, N_2 , to produce a fourth coherent-radiation photon with an anti-Stokes frequency ω_3 . The total spectrum of emitted frequencies of scattered light has a complex shape dependent on temperature, whose value is usually estimated through a comparison between the experimental spectrum and a set of spectra calculated for various temperatures.

Since it normally takes several minutes to register a CARS spectrum by scanning the frequency ω_2 of narrow-band radiation emitted by a frequency-tuned laser, this method can only be applied to stationary processes [1]. Stufflebeam and Lefebvre [2] used wide-band emission from a powerful dye laser to simultaneously excite the whole spectrum of frequencies ω_3 with the help of one pulse of a 10^{-8} sec duration. In the present work, we used a dual-line version of the CARS method whose implementation does not require high energy parameters of lasers. In this method, instead of measuring the total CARS spectrum, one has to excite and register scattered light at only two frequencies to determine the instantaneous combustion temperature in the region where the laser beams cross each other [3].

The purpose of the present work was to develop a dual-line CARS technique for measuring the combustion temperature of a model propellant — a stoichiometric ammonium dinitramide–polycaprolacton mixture whose combustion products contain nitrogen. The burning time of a propellant specimen was about 0.5 sec at a measurement-volume pressure of 4 MPa.

Calculation of CARS spectra. The temperature was determined from the spectral shape of the Q-branch $0 \rightarrow 1$ vibration band ($\Delta v = +1$ and $\Delta J = 0$) of nitrogen, which consisted of several closely spaced lines (v and J are the vibrational and rotational quantum numbers). The CARS intensity can be determined from the formula

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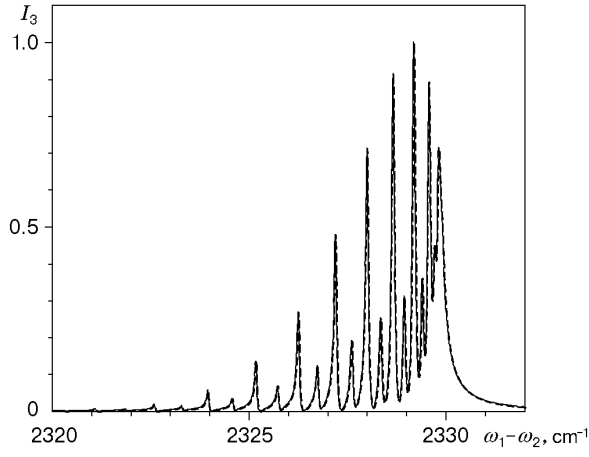


Fig. 1

Fig. 1. CARS spectra of N_2 measured at $p = 0.1$ MPa and $T = 294$ K: the solid curve presents calculations and the dashed curve shows the experimental data of [6].

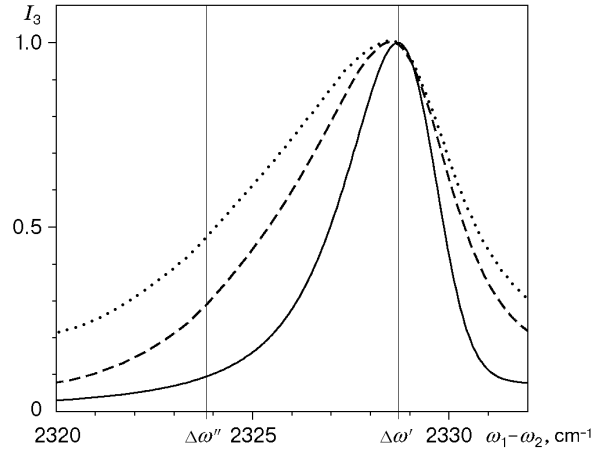


Fig. 2

Fig. 2. Calculated CARS spectra of N_2 at $p = 4$ MPa and $T = 300$ (solid curve), 1800 (dashed curve), and 3300 K (dotted curve).

$$I_3 = (4\pi^2\omega_3/c^2)^2 |\chi^{(3)}|^2 I_1^2 I_2,$$

where I_1 and I_2 are the intensities of the laser beams and c is the speed of light. The nonlinear cubic susceptibility consists of non-resonance and resonance parts [4]:

$$\chi^{(3)} = \chi^{nr} + \chi^r = \chi^{nr} + \chi' + i\chi'',$$

where

$$\chi^r = \sum_{v,J} \frac{R_{v,J}}{\Omega_{v,J} - (\omega_1 - \omega_2) - i\Gamma_J},$$

$\Omega_{v,J}$ is the optical-transition frequency, Γ_J is the half-width of the line, $R_{v,J} = (2N/\hbar)(c/\omega_2)^4 \times (d\sigma/d\Omega)(v+1)b_{J,J}\Delta_{v,J}$ is the transition intensity, N is the number density of molecules, \hbar is the Planck constant divided by 2π , $d\sigma/d\Omega$ is the spontaneous-scattering cross section, $b_{J,J} = J(J+1)/((2J-1)(2J+3))$ are the Placzek–Teller coefficients, and $\Delta_{v,J} = n_{v,J} - n_{v+1,J}$ is the difference in populations of molecular levels between which the optical transition occurs.

With due regard for the Boltzmann distribution of electrons on the molecular levels, the population versus temperature dependence acquires the form

$$n_{v,J} = \frac{1}{Q} g_J (2J+1) \exp\left(-\frac{(G_v + B_v J(J+1))hc}{kT}\right),$$

where Q is the statistical sum over all states, g_J is the statistical weight due to nuclear spin, G_v is the vibrational term, B_v is the molecular rotational constant, k is the Boltzmann constant, and T is temperature. As was shown in [5], the line interference effects in the Q-branch $0 \rightarrow 1$ band can be taken into account by representing the imaginary part of the susceptibility in the form

$$\chi''(J) \sim p \frac{\gamma_J - ((\omega_1 - \omega_2) - \Omega_{v,J})Y_J}{(\Omega_{v,J} - (\omega_1 - \omega_2))^2 + (p\gamma_J)^2},$$

where p is the pressure. The values of the coefficients of line broadening γ_J and of the so-called line mixing Y_J for N_2 are given in [5]. Using the above formulas, one can calculate the shape of CARS spectra of nitrogen.

Figure 1 shows a CARS spectrum obtained experimentally [6] and a CARS spectrum calculated for $T = 294$ K and $p = 0.1$ MPa; Fig. 2 shows a family of CARS spectra of pressurized nitrogen, calculated for various temperatures.

Experimental Procedure. The solid-propellant specimen was burnt in a special chamber filled with a buffer gas ($p = 4$ MPa). To admit the probing beams into the chamber and perform observations, the chamber was provided with optical windows. The burning at elevated temperatures and pressures caused some distortions of laser beams because of a large gradient of the refractive index at the border of the combustion-products jet,

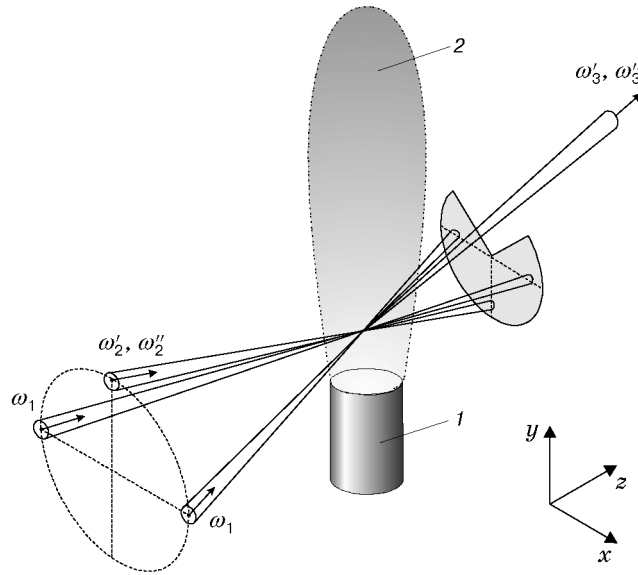


Fig. 3. Diagram of laser beams: solid-propellant specimen (1) and flame (2).

which resulted in attenuation of the CARS signal and even in its disappearance. That is why, as a buffer gas, we used helium, which had almost the same refractive index as the high-temperature combustion products. A cylindrical specimen of the propellant (10 mm in diameter and 10 mm high) was installed vertically at the center of the chamber. The specimen was ignited from its top face with the help of an ohmically heated Nichrome wire. The pressure in the gas system was maintained constant within 5%.

For the two-frequency excitation of the CARS signal in the tunable-laser emission spectrum, two narrow lines with Stokes frequencies ω'_2 and ω''_2 were excited. As these line interacted with the radiation at the main frequency ω_1 , two lines with anti-Stokes frequencies $\omega'_3 = 2\omega_1 - \omega'_2$ and $\omega''_3 = 2\omega_1 - \omega''_2$ appeared in the CARS spectrum. The ratio between the signals at the frequencies ω'_3 and ω''_3 was used to calculate the flame temperature.

The source of coherent radiation with the frequency ω_1 was a Q-switched solid-state Nd:YAG-laser, with conversion of its emission into the second harmonic (wavelength 532 nm, pulse energy 70 mJ, and pulse duration $2 \cdot 10^{-8}$ sec). The repetition frequency of the pulses was 10 Hz. Some part of the output energy of the Nd:YAG-laser (60%) was used to pump a tunable 6-aminophenalenon dye laser with a prismatic dispersion element installed in its resonator (the wavelength was approximately 607 nm, pulse energy 8 mJ, and pulse duration $1.5 \cdot 10^{-8}$ sec). Two beams of equal intensities (Fig. 3), obtained by dividing the remaining part (40%) of the solid-state laser radiation, and also the beam from the tunable laser were focused and drawn together with the help of an optical lens (focal length $f = 390$ mm), thus forming a measurement volume ($0.15 \times 0.15 \times 6$ mm). The CARS beam thus formed in the measurement volume was focussed on the entrance slit of the spectrograph ($f = 820$ mm), a double monochromator DFS-24. In the exit focal plane of the monochromator, a computer-controlled multichannel spectrum analyzer was installed, which consisted of an intensity amplifier and a photodiode array (1024 elements 0.15×25 mm). The contribution of non-resonance susceptibility to the measured signal was suppressed by proper orientation of polarizations in the pumping beams (0 for ω_1 and $+60^\circ$ for ω_2), and also by introducing the analyzer into the anti-Stokes beam (-60° for ω_3).

The frequencies and intensities of dye-laser emission were adjusted using the above-described registration system equipped with a high-pressure chamber. The pressure in the chamber was increased from 0.1 to 4 MPa through adding helium ($p = 3.9$ MPa) to the air initially present in it. Through adjustment of the dye-laser wavelength, a maximum level of the anti-Stokes signal was achieved. Afterwards, a Fabry-Perot etalon with a base of 1.03 mm was installed in the resonator of the tunable laser. The frequency difference between the neighboring transmission peaks of this interferometer was 4.84 cm^{-1} . These conditions reduced the laser linewidth from 1 to 0.1 cm^{-1} . By titling the etalon, the tunable-laser emission line in the N -th order transmission peak was matched to the envelope maximum of the Q-branch resonance nonlinear susceptibility of N_2 , in which the Raman shift is $\Delta\omega' = \omega_1 - \omega'_2 = 2328.69 \text{ cm}^{-1}$ (see Fig. 2). On readjusting the resonator frequency into the short-wavelength spectral region, simultaneously with a decrease in the laser-line intensity, a second line appeared

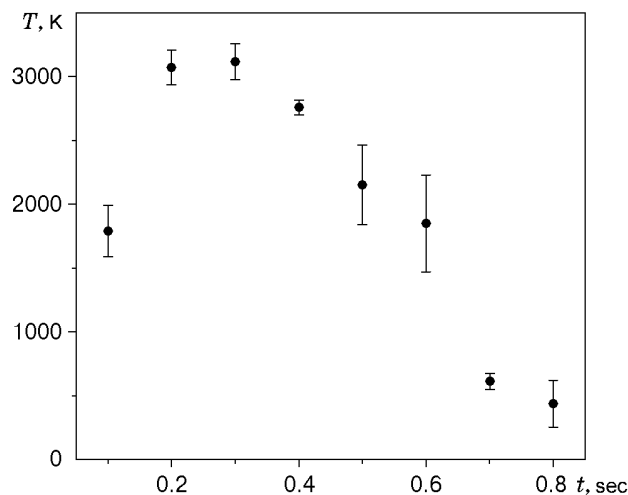


Fig. 4. Mean temperature versus burning time.

at the frequency of the next transmission peak of the Fabry–Perot etalon, which corresponded to the Raman shift $\Delta\omega'' = \omega_1 - \omega_2'' = 2323.85 \text{ cm}^{-1}$. The intensities of the lines with the frequencies ω_2' and ω_2'' were equalized.

Measurement Data. Preliminarily, the dye-laser emission spectrum was recorded by averaging 25 measured intensities at each wavelength. The obtained amplitudes of the signals at the lines were subsequently used to apply a correction to the intensities of signals at the anti-Stokes frequencies. Then, at $T_0 = 293 \text{ K}$, we registered a “reference” dual-line CARS spectrum of nitrogen with the same number of measurements performed at each wavelength. The initial distance between the measurement volume and the surface of the specimen to be ignited was about 1 mm. After complete change of the chamber gas for helium, the specimen was ignited under a working pressure of 4 MPa, and CARS spectra from each laser flash were registered at a frequency of 10 Hz. The onset of burning was identified, with a 0.1-sec accuracy, by the appearance of a low-intensity flame-induced background in the CARS spectra. During the time interval from the moment of specimen ignition till the moment by which the chamber was filled with non-transparent combustion products, we could register 5–6 CARS spectra.

The procedure was tested in experiments on measuring the gas temperature [$T = (1174 \pm 60) \text{ K}$] at the axis of a Nichrome spiral, which was a coil wound from a 0.15 mm diameter wire (winding length 10 mm, inner diameter 2.5 mm, pressure 4 MPa, and volume fraction of nitrogen 0.02). The coil was ohmically heated to a temperature of $(1273 \pm 5) \text{ K}$, registered with the help of a pyrometer with vanishing wire.

The measurements were performed in 14 combustion tests. In data processing, a calculated temperature dependence of the ratio between the CARS intensities at the two above-indicated frequencies was used. Figure 4 shows the time dependence of the mean temperature obtained by averaging the whole set of data gained. In the experiments, the random error of a single measurement, which amounted to 500 K, was induced by the photodetector’s Schottky noise and by the laser-power fluctuations arising under conditions without any normalization of the measured signal to the pulse power. The temperature obtained by averaging the measured values over nine instantaneous measurements performed in the time interval from 0.2 to 0.3 sec is $3097 \text{ K} \pm 3\%$. This value of the rotational temperature of nitrogen in the reaction-products jet corresponds to a 5-mm increase in the distance between the flame front and the measurement volume. With due regard for the actual value of the chamber pressure, a rough equality between the rotational and translational temperatures in the measurement region may be assumed. A possible systematic error in the measurements could arise owing to inaccuracies in the calculation of CARS spectra according to the model used.

In conclusion, a technique for local optical measurements of the combustion temperature of substances whose combustion products contain nitrogen was developed. This technique may prove useful in synthesizing solid propellants and diagnosing their combustion.

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