High-speed Measurement of Vibrational and Rotational Temperatures of Nitrogen Molecules behind Hypervelocity Shock Wave by CARS Method

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In the re-entering phase of space vehicle into the atmosphere strong shock wave is generated in front of the hypersonic vehicle, and high enthalpy flow with radiating, non-equilibrium real gas effects is generated behind the shock wave. As well as usual convecting heat transfer, the radiative and non-equilibrium real gas heating from the shock-heated air ahead of the vehicle plays an important role on the total heat flux to the wall surface, which affects the heat shield design of the re-entering vehicle. As for the research of such non-equilibrium high enthalpy flows behind strong shock waves, several spectroscopic studies have been reported by using shock tubes or shock tunnels. The direct measurement, however, of molecular vibrational/rotational temperatures from ground state, has not been performed, and the experimental data are in quite insufficient conditions. In this paper nonlinear spectroscopic measurement is performed on the vibrational/rotational temperatures of nitrogen behind the hypervelocity shock waves from 4-5km/s by CARS method. The CARS spectroscopic signals have been successfully observed by free-piston, double-diaphragm shock tube experiments, and the measured results are compared with the simulated spectra to decide the temperatures by spectral fitting method.

Key Words: CARS, Hypervelocity Shock Wave, Vibrational and Rotational Temperatures, Nitrogen Molecule, Spectral Fitting

1. Introduction

The radiative high enthalpy flow is of great importance in the research of heat shield problems for re-entering space vehicles into the atmosphere. The non-equilibrium flow with radiative and real gas effects from the shocked air ahead of the vehicle plays an important role on the total heat flux to the wall surface as well as usual convective heat transfer. In order to clarify the radiative and non-equilibrium characteristics of the strongly shocked air, many experimental studies have been carried out during the last decades by the researchers using shock tube devices^{1), 2)}.

In our previous works a CCD camera system was introduced in the radiation observation of hypervelocity shock waves in low-density air³⁾ with an imaging spectrograph, a streak camera, or a gated image-intensified CCD (ICCD) camera and personal computer. Some interesting features were obtained independently for the total radiation and for the spectral radiation behind shock waves with velocity over 10 km/s in air⁴⁾. Based on these experimental results, we also used the Boltzmann plot method related to the second positive band of nitrogen molecules to evaluate vibrational/rotational temperatures of the molecule from the time-resolved spectroscopic data. The Boltzmann plot method, however, was based on several assumptions, and the method suffered from experimental peak to peak errors and measured data of the activation from different state levels apart from ground state of observed molecules.

On the other hand, as for the combustion experiments, Coherent Anti-Stokes Raman Spectroscopy (CARS) method

has been developed for temperature and concentration measurement method^{5), 6)} in connection to the number density of observed species. The CARS has been successfully used with a nonlinear, four-wave optical mixing technique for high temperature flows, combustion, and so on^{7), 8), 9)}. The CARS system also produces a strong and coherent signal that can be detected even in the strong background luminosity.

In our study CARS measurement of vibrational/rotational temperatures of nitrogen molecules in hypersonic air flow behind the strong shock waves has been established over 5 km/s shock velocity¹⁰⁾. The CARS signal could be successfully acquired from the non-equilibrium hypervelocity flow behind the strong shock waves with 10ns gate range. In this paper the measured CARS results for shock waves from 4km/s to above 5km/s are reported. In addition, these spectroscopic data are compared with the theoretical spectroscopic data, and vibrational/rotational temperatures are evaluated for different shock wave velocity by spectral fitting method. We also have evaluated the spectral matching errors to improve the reliability of our CARS experiments.

2. CARS Method and Calculation

CARS is one of the Raman spectroscopy methods. This method is spectroscopic diagnostics which can determine the vibrational/rotational temperatures and chemical species concentration. This spectroscopy method corresponds to the scattering phenomena for nonlinear response of the medium to electromagnetic wave. In CARS method two lasers are irradiated to a sample, then the strong emission intensity by

scattering process is generated. The CARS has such features that the scattered light intensity is very high of $10^5 \sim 10^{10}$ times than Raman scattered light intensity, and the signal is emitted in one direction as a laser beam, so the CARS has high space-time resolution. It has, however, issues that the arrangement of optical system and temporal matching are very much complicated and difficult.

The theory of the CARS effect has been developed extensively. Incident laser beams at frequencies ω_1 (pumping beam) and ω_2 (Stokes beam) interact through the third order nonlinear electric susceptibility $\chi^{(3)}_{\text{CARS}}$ of the gas molecule to produce coherent radiation (ω_3) at $\omega_3 = 2\omega_1 - \omega_2$ as follows;

$$I_3(\omega_3) = \frac{\omega_3^2}{n_1^2 n_2 n_3 c^4 \epsilon_0^2} |\chi^{(3)}_{\text{CARS}}|^2 I_1^2(\omega_1) I_2(\omega_2) l^2 \left(\frac{\sin \frac{\Delta k l}{2}}{\frac{\Delta k l}{2}} \right)^2 \quad (1)$$

$$\Delta k = 2k_1 - k_2 - k_3 \quad (2)$$

where n_1 , n_2 and n_3 are the refractive index at ω_1 , ω_2 , ω_3 , respectively; c is the velocity of light; l is interaction length; k_1 , k_2 and k_3 are the wave vectors of the pumping, Stokes, and CARS beams, respectively; ϵ_0 is the permittivity of free space. The CARS signal is enhanced on the condition of phase matching, $\Delta k = 0$. Then the four vectors form a phase-matching diagram (BOXCARS) shown in Fig.1. The incident laser beams, i.e. two pump beams (k_1) and a Stokes beam (k_2), are aligned in order to satisfy this vector relation. In this state the CARS signal can be obtained at high signal intensity. Moreover, emission intensity is proportional to the cube of incident beam (the square of pump beam and the first power of Stokes beam). $\chi^{(3)}_{\text{CARS}}$ is shown by

$$\chi^{(3)}_{\text{CARS}} = \sum_j K_j \frac{\Gamma_j}{2\Delta\omega_j - i\Gamma_j} + \chi_{nr} \quad (3)$$

where the j summation is over vibration-rotation transitions in the vicinity of $\omega_1 - \omega_2$; Γ_j is the Raman line width (FWHM); χ_{nr} is a background contribution due to electrons and remote resonances; and $\Delta\omega_j$ is shown to be related to the Raman cross-section by⁹⁾

$$K_j = \frac{2n_1 c^4}{n_2 \hbar \omega_2^4} N \Delta_j \left. \frac{d\sigma}{d\Omega} \right|_j \Gamma_j^{-1} \quad (4)$$

where $\hbar$ is h divided by 2π , N is the number density of the Raman active molecule, Δ_j is the population difference between the upper and lower vibration-rotation states, and $(d\sigma/d\Omega)|_j$ is the cross-section for spontaneous Raman scattering.

On the assumption that molecules have Boltzmann distributions based on the rotational (T_r) and vibrational (T_v) temperatures, Δ_j can be expressed as

$$\Delta_j = \frac{(2J+1)g_J}{Q_r Q_v} \left[\exp\left(-\frac{F_{v,J} hc}{kT_r}\right) \exp\left(-\frac{G_v hc}{kT_v}\right) - \exp\left(-\frac{F_{v+1,J} hc}{kT_r}\right) \exp\left(-\frac{G_{v+1} hc}{kT_v}\right) \right] \quad (5)$$

where $F_{v,J}$ and G_v are the rotational and vibrational energy terms, respectively; g_J is the spin degeneracy, 6 for even- J rotational levels and 3 for odd- J levels in N_2 ; and Q_r and Q_v are the rotational and vibrational partition functions, respectively.

From Eqs. (1), (3) and (4), CARS signal may be approximately proportional to the square of number density of molecule. Therefore, it is not easy to detect the CARS signal especially from low-pressure and radiating gas of fast velocity. Figure 1 is the vector diagram of BOXCARS. When this vector relation is attained in each pumping laser beams k_1 and Stokes beam k_2 , the measured CARS signal k_3 becomes coherent and strong.

As written in the following section, the measured CARS spectra are fitted with calculated CARS spectra by treating T_r , T_v , Γ as free parameters to decide the temperatures.

Fig. 1. Phase-vector diagram of BOXCARS

3. Spectral Fitting Method for Temperature Estimation

CARS spectroscopic data obtained by our experiment relate to the energy levels which correspond to the kinetic conditions of the molecule. Vibrational/rotational temperatures are determined by fitting the computer-generated and theoretical spectra to the observed CARS spectra. The spectral fitting method is explained as follows. First, theoretical spectra are developed by the computer program, which includes the vibrational/rotational temperatures, the Raman line widths and non-resonant parameters, and these parameters are varied in the assigned bounds. Secondly, square mean errors of normalized emission intensity between the computer-generated theoretical spectrum and observed CARS spectrum are calculated, and finally vibrational/rotational temperatures of nitrogen molecule are determined, where the error become minimum.

Raman line width corresponds to the half width at half maximum of Raman line, and the function of pressure, temperature and rotational quantum number of the molecule. Non-resonant parameter is the constant, unconcerned element about Raman resonance.

4. Experimental Apparatus and Diagnostic System

In CARS experiment we have used a free-piston, double-diaphragm shock tube to generate the strong shock waves in low-density gas as shown in Fig.2¹¹⁾. This shock tube consists of high-pressure tube (driver gas is nitrogen), compression tube (helium gas is supplied), buffer tube (supplied gas is also helium), low-pressure tube (test gas is air or nitrogen), and vacuum chamber. The each tube is divided off by a quick action valve, the first diaphragm (steel), and the second

Two pumping beams and Stokes beam are focused into shock tube through a focal lens. The path of laser beams and CARS beam are shown in Fig.4. In this case phase-matching condition has to be satisfied as well as planer BOXCARS. This method is called as folded BOXCARS, especially as multiplex folded BOXCARS using broadband Stokes beam at single shot. This method has the advantage in separating CARS signal from pumping and Stokes beams.

In this study the synchronization of the shock wave and laser beams is very difficult to apply CARS method from the hypervelocity flow behind the strong shock wave. In this study, as the shock wave velocity ranges over 4-5km/s, measurement accuracy should be within on order of μs .

The three beams (ω_1 and ω_2) must be irradiated on time when the shock wave running over 5 km/s just arrives at the observation window. The trigger system for synchronizing laser beams with shock wave is shown in Fig.5. In this figure the charge and fire (flash) trigger signals are constantly applied with designated interval as indicated in dashed lines, and then at the shock tube operation real trigger system is applied as shown in solid lines. The Nd: YAG laser is controlled by external signals. To begin with, a charge trigger is applied for flash lamp in YAG laser. After the fire trigger a Q-switch trigger opens Q-switch, and starts the laser beam irradiation. Before the measurement the charge and flash triggers are repeated at 10Hz. To produce the shock wave, the

Fig. 4. Laser beams CARS path (top view and side view)

Fig. 5. Outline of the trigger system synchronizing laser beams with hypervelocity shock wave

starting valve installed in a high-pressure tube is opened, and simultaneously the signal sends a charge trigger to the YAG laser. When shock wave arrives at a pressure transducer on the buffer tube, a delay pulse generator is triggered. Finally, DPG1 is triggered by short-circuit of an ion probe with shock wave passing, and sends a Q-switch trigger to YAG laser. As shown in Fig. 5, DPG1 sends simultaneously triggers to the ICCD for detecting CARS signal.

5. Experimental Results and Discussion

In this paper the measured spectral data are presented at 2666Pa and 1333Pa initial pressures. Reliability is evaluated for the measured spectra at 2666Pa initial conditions. After comparing of spectral data by different shock wave velocities, the spectral fitting for each spectrum has been conducted.

The measured image of CARS signal is shown in Fig.6. Test gas is room air, and velocity of shock wave is 4.14km/s with Mach number of 12.04. The measurement position is 5.1mm behind the shock front. Initial pressure is 2666Pa. Horizontal axis is wavelength and vertical axis is equivalent to the height of incidence light into the slit of spectrograph. The color is corresponding to the strength color bar on the right side. As shown in Fig.6, the clear image is taken without strong noise. Background light of YAG laser can be cut well.

Fig. 6. Measured ICCD image of CARS signal

5.1. Reliability of the spectrum

Figure 7 shows the measured spectroscopic data. Horizontal axis is wave number and vertical axis is normalized emission intensity. The measured spectrum, Experiment1, corresponds to the image of CARS signal of Fig.6. Shock wave velocity of Experiment2 is 4.07km/s, Mach number of 11.84. The measurement position is 5.05mm behind the shock front. Initial pressure is 2666Pa. As the experimental conditions are almost similar to both spectral data, reliability of the spectrum can be confirmed from these data. The spectral shape corresponds each other over 21150cm^{-1} of spectrum range, without considering the non-resonant part. The peak and depth values and their wave numbers coincide well. In Experiment2 some noises are observed, so there are some differences of spectra to be influenced. Therefore, these spectra are swayed in some amount by background noises. Though the same

experimental conditions are difficult for us to obtain, reliable data can be observed if clear spectral image is taken at same experimental conditions. So, the clear spectroscopic images without strong noises are needed to avoid mismatch in the spectral fitting procedure.

5.2. Comparison of the spectral data by shock wave velocity

The CARS spectrum of shock wave velocity of 4.14km/s (same as Experiment1 of Fig.7) is compared in Fig.8 with another spectrum from stronger shock wave velocity of 5.22km/s, where the measurement position is 6.47mm behind the shock front, Mach number is 15.1, and initial pressure is 1333Pa. The number of peaks is almost same, and the normalized height of peaks and depth of concaves agree partially, but the spectral data of shock wave velocity 5.22km/s shows totally larger intensity distribution. Especially, it is apparent that the spectrum of shock wave velocity 5.22km/s shows higher intensity at around 21030 and 21100 cm^{-1} . It is not yet clarified which is the main cause between the difference of measuring positions behind the shock front, and difference of shock wave velocities, or simple error. Significant difference can be seen in non-resonant part

Fig. 7. Experimental spectra under the same experimental conditions

Fig. 8. Experimental spectra by shock wave velocity
(Initial pressures: 2666 Pa and 1333 Pa.)

above 21150 cm^{-1} in these spectra. This part is clearly found at the spectrum of shock wave velocity of 5.22km/s, but is not found in the spectral data for shock wave velocity of 4.14km/s. Non-resonant part seems to be eliminated by reducing shock wave velocity 1 km/s. In this way the difference and feature of the measured spectra are figured out, but it is still unclear that the difference is originated from the different vibrational and rotational temperatures. So, they will be studied hereafter.

5.3. Temperature diagnostic result (Mach number 15)

The measured spectroscopic data together with theoretical spectrum are shown in Fig.9. The measured data are the same as the spectrum of shock velocity 5.22km/s in Fig.8 with 6.47mm behind the wave front. The theoretical spectrum was calculated with varying four parameters, T_v , T_r , Γ and χ_{nr} . After the fitting, the vibrational and rotational temperatures are estimated to be 4500K and 4500K, respectively. The measured spectrum successfully corresponds to the theoretical spectrum between 21030 cm^{-1} and 21100 cm^{-1} . Some mismatch can be seen at lower 21030 cm^{-1} and higher 21100 cm^{-1} . Then, there exists large discrepancy at non-resonant part more than 21130 cm^{-1} . If theoretical spectrum is recalculated to match the difference, new mismatch is generated in other parts. So, the parameters in the fittings program should be configured by more precisely setting.

Fig. 9. Fitting of calculated spectrum to experimental spectrum
(Initial pressure:1333 Pa)

5.4. Temperature diagnostic result (Mach number 12)

The measured spectral shape with theoretical spectrum is shown in Fig.10. This is same as the spectrum Experiment1 of lower velocity in Fig.7 with 5.1mm behind the wave front. The theoretical spectrum has been calculated with varying four parameters, T_v , T_r , Γ and χ_{nr} . After the fitting, the vibrational and rotational temperatures are estimated to be 5000K and 5500K, respectively. In the same way as the result of shock wave velocity 5.22km/s, the measured spectra can successfully correspond to the theoretical spectrum between 21050 cm^{-1} and 21100 cm^{-1} . Some discrepancy, however, is found around the peaks of 21030 cm^{-1} and 21120 cm^{-1} . The spectra are absolutely corresponding over 21150 cm^{-1} of spectrum, even without non-resonant part. Agreement in

higher wave number range means more accurate temperature results in our experiment. It is expected that vibrational and rotational temperatures at no non-resonant part are higher than existing non-resonant part. This is because that the measurement locations are different.

Fig. 10. Fitting of calculated spectrum to experimental spectrum (Initial pressure: 2666 Pa)

6. Summary

The CARS signals have been successfully observed at shock wave velocity range from 4km/s and over 5km/s. The measured spectra agree well with the theoretically fitting spectrum. Vibrational and rotational temperatures are decided for nitrogen molecules in air behind the strong shock wave front by the spectral fitting method. Reproducible data can be obtained at similar experimental conditions. The spectrum that does not indicate the non-resonant part has been obtained at initial pressure of 2666Pa for Mach number around 12. The nitrogen molecules in strongly shock-heated air come to these non-equilibrium states between shock front and measured positions with vibrational/rotational temperatures of much lower values than the translational temperature. In our experimental results the nitrogen molecules would come to near ro/vibrational equilibrium situation behind the shock front, because the vibrational temperature almost corresponds to the rotational temperature in shock wave velocity 5.22km/s, with 6.47mm behind shock front, and shock wave velocity 4.14km/s, 5.1mm behind shock front. It is necessary to compare each temperature at non-equilibrium state with different stronger shock wave velocities with varying the measuring positions behind the strong shock wave front.

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