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Techniques for Estimating Rotational and Vibrational Temperature in Nitrogen Arcjet Flow

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Molecular nitrogen and molecular nitrogen ion spectra are used to infer vibrational and rotational temperatures in an arcjet shock layer under the assumption of Boltzmann populations. Various techniques correlate spectral features with temperatures, among which are determining intensity integrals and forming ratios that are then correlated with rotational and vibrational temperatures. Sensitivity factors, determined by correlating these ratios with temperature, are indicators of the potential accuracy of different spectrum regions for determining temperature. In another technique, least-squares fits of measured spectra are made to fit temperature-dependent computed spectra, including global fits to computed spectra as a function of temperature or fits to vibrational-level basis spectra. Technique accuracy is described and precision improved by combining the results of several techniques. When results from the various techniques are combined, overall temperature determination accuracy at a single point in an arcjet shock layer is about ±4% for vibrational temperature and ±10% for rotational temperature.

Nomenclature

B = I_P/I_R
f_{ij} = sensitivity factor
I = intensity
J = rotational quantum number
K' = rotational quantum number of upper state
K'' = rotational quantum number of lower state
R_{ij} = ratio of intensity integrals for ranges i and j
T_r = rotational temperature
T_v = vibrational temperature
v' = vibrational quantum number of upper state
v'' = vibrational quantum number of lower state
λ_1 = lower wavelength of range
λ_2 = upper wavelength of range

Subscripts
c = computed
exp, e = measured
i, j = wavelength range designations
P, R = rotational spectrum branch designations
z = with background subtracted

Introduction

INTEREST is increasing in characterizing arcjet flows used to determine thermal protection material behavior. Arcjet flow parameters are necessary to improve the correlation of material performance with flow composition and to determine catalytic recombination coefficients. Various emission spectroscopic techniques[1–7] have been used to determine temperatures and vibrational population distributions of N_2 and N_2^+ in arcjet flows. These offer advantages or disadvantages, depending on measured spectra resolution, temperature range, overlapping contributions from various species, and the possibility of vibrational nonequilibrium. The flow in arc jets generally may be significantly out of chemical and thermal equilibrium, which limits our ability to infer temperature. Yet in cases where the pressure is relatively high, e.g., in the plenum or normal shock layer of a test article, it may be possible to infer temperatures. We approached the subject of determining temperature from this perspective. Nonequilibrium effects are investigated in a companion paper.[8] In this paper we will address only cases where thermal equilibrium within an energy mode is obtained. Ideally, to determine the rotational temperature we should use very high resolutions, which ensure that individual rotational lines are resolved; but in this case, Boltzmann plots may be used. With such a resolution, in principle, we could also isolate the various spectrum components associated with individual vibrational levels to make Boltzmann plots for determining vibrational temperature. Because of the complexity of nitrogen molecular spectra and practical considerations such as minimization of data acquisition time and cost, one usually must compromise to determine the vibrational population distribution and temperature from less-resolved measurements. Another difficulty is that the higher the temperature, the less sensitive the spectra become to temperature. Arcjet shock-layer flows typically are above 4000 K, where the spectrum is less sensitive to temperature. This paper discusses several techniques that may be used between 4000 and 10,000 K and gives

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estimates of accuracy. These techniques are applied to radiation emitted from the shock layer of an arcjet flow around a quasi-two-dimensional body in the arcjet materials test facility at NASA's Johnson Space Center. The objective of this paper is to investigate various methods of determining rotational and vibrational temperatures by measuring the emission spectra of nitrogen and give an indication of sensitivity and accuracy. The companion paper[8] discusses applying these techniques to determine temperature distribution in the shock layer of an arcjet flow, although we determined that significant nonequilibrium exists. If the arcjet flow contains oxygen, such as is used to simulate air, determining rotational temperature from the NO spectrum might also be possible.[9]

Spectroscopic Techniques for Determining Temperature

In flows where T_v and T_r are not expected to be the same, spectra must be treated assuming that these temperatures will differ. If possible, techniques must be used that are independent of each other. These techniques are evaluated here in terms of accuracy required and independence of the T_r determination from knowledge of T_v, and vice versa. The spectra studied in this paper have been observed in the shock layer of a blunt-body in arcjet flow. Electronic transitions resulting from the spectra are shown in the energy-level diagram for N_2 and N_2^+ (Fig. 1); vibrational states are shown schematically in the figure inset. It should be pointed out that emission spectra yield information about the upper or excited state; therefore, temperatures obtained from these spectra are not associated with the much more highly populated ground state. It is only by assumption that we can associate the inferred temperature with that of all states of the molecule.

Rotational Temperature of N_2^+ from Nonfully Resolved Spectra

Techniques for determining the rotational temperature of various electronically excited states of N_2^+ are grouped into four methods: 1) The ratio of intensity integrals; 2) allocation of R and P branches in the $(v', v'') = (0, 1)$ spectrum (transitions from upper electronic state with vibrational-level v' to lower electronic state with vibrational-level v''); 3) least-squares for minimizing the difference between measured and calculated rotational features of the $B^2\Sigma_u^+ - X^2\Sigma_g^+$ (0, 1) spectrum; and 4) minimizing deviations between computed and measured spectra, with T_r as a parameter.

Although bands other than (0, 1) could be analyzed, the (0, 1) band acts as a compromise between intensity, separation of rotational features, and a lack of significant background. The (0, 0) band is stronger, but its rotational spectrum is less resolved. The (1, 2) band may be better resolved, but it is much weaker.

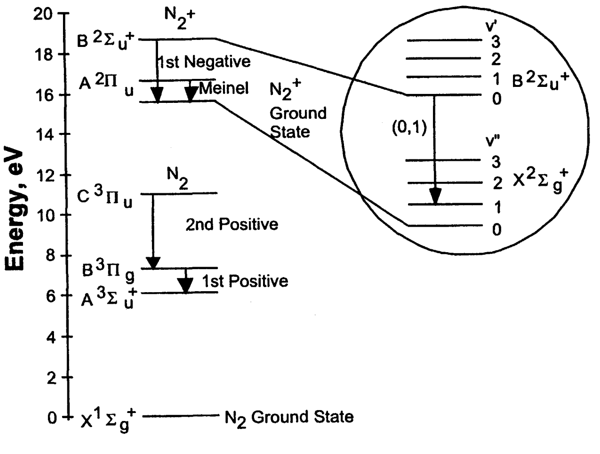

Fig. 1 Energy-level diagram and definition of states studied in this paper.

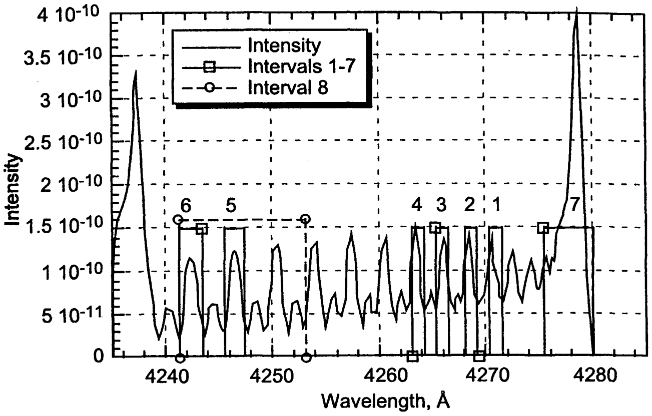

Fig. 2 Measured spectrum of N_2^+ (0, 1) rotational structure at a relatively low resolution. Intensity integral wavelength intervals are shown.

Ratio of Intensity Integrals in the N_2^+ B-X (0, 1) Spectrum

The ratio of integrated intensities method uses small wavelength intervals within a rotational band.[10] More recently, Blackwell et al.[2] and Park et al.[9] used this method to analyze the rotational spectrum in a wavelength range of 424–428 nm. Although integration may take place over many wavelength ranges, Park et al.[9] showed that a larger spread in wavelengths or rotational quantum numbers results in greater accuracy. In particular, we have used several wavelength ranges, as shown in Fig. 2 and Table 1. We also show the sensitivity factors associated with various ratios. The sensitivity factor f_{ij} is defined in terms of the ratio of intensities $R_{ij} = I_i/I_j$. The relative change in ratio to the relative change in temperature can be expressed mathematically as

$$f_{ij} = \frac{d\ell n(R_{ij})}{d\ell n(T)} \approx \frac{\Delta R_{ij}/R_{ij}}{\Delta T/T} \tag{1}$$

It can be shown that a function of the form

$$R_{ij} = I_i/I_j = T^{f_{ij}} \tag{2}$$

exactly satisfies Eq. (1). Using this function, a global approximation of f_{ij} can be found by assuming that R_{ij} depends on T. The calculated integral intensity ratios vs T are then curve fit to the function to determine its sensitivity, f_{ij}. If $f_{ij} = 0.5$, a 10% error in I_i/I_j will result in a 20% error in T. In other words, the larger f_{ij} the smaller the error in T will be.

An example of determining the sensitivity factor for the N_2^+ (0, 1) transition rotational structure is considered in Fig. 3, where the ratio of intensities for ranges 8 to 7 is plotted. Sensitivity factors determined from fits of Eq. (2) to the calculated intensity integral ratios are shown as exponents in the figure. Note that the integrals may include a background continuum, if present. The ratios are therefore calculated with the background subtracted from the intensities; and the background is determined by fitting a straight line to the spectrum in a region at a higher wavelength, adjacent to the region of interest for the (0, 1) transition. The wavelength range used to determine the background here is given in Table 1. The sensitivity factor $f_{87} = 0.5175$ when the background is subtracted. Sensitivity factors for other integral intensity ratios are also given in Table 1. Note that, although the greatest sensitivity is for the ratio I_6/I_7, the accuracy of I_6 significantly depends on matching wavelengths. Because a wavelength error will affect the value of the integral, a wider range, range 8, is preferred, even though its sensitivity factor is somewhat smaller. Figure 3 shows the ratio of range 8 to range 7, with and without background.

Table 1 Wavelengths for intensity integrals used for T_r determination for the (0, 1) bandhead region

Background range, nm			Integral ranges, nm			Sensitivity factor, f_{ij}	
λ_{b1}	λ_{b2}	Range no.	λ_1	λ_2	Integral ratios	w/o background subtraction	w/ background subtraction
428.30	429.50	1	427.03	427.15	1/7	0.230	0.198
——	——	2	426.81	426.93	2/7	0.272	0.241
——	——	3	426.53	426.65	3/7	0.251	0.255
——	——	4	426.30	426.42	4/7	0.313	0.282
——	——	5	424.55	424.74	5/7	0.491	0.429
——	——	6	424.121	424.331	6/7	0.537	0.462
——	——	7	427.55	428.00	8/7	0.518	0.409
——	——	8	424.121	425.30	——	——	——

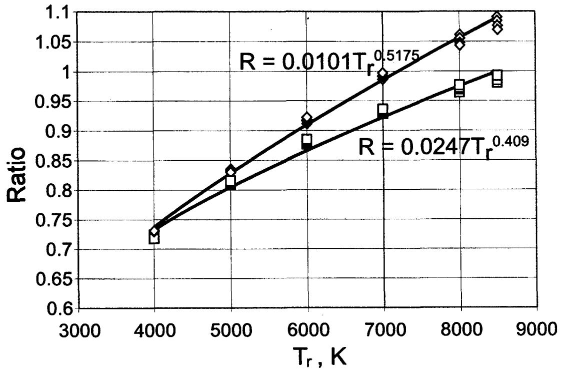

Fig. 3 Ratio of intensity integrals vs T_r for T_r in the range 4000–10,000 K. Wavelength intervals 8 to 7 of the (0, 1) system (see Table 1) with (upper curve) and without (lower curve) background subtraction.

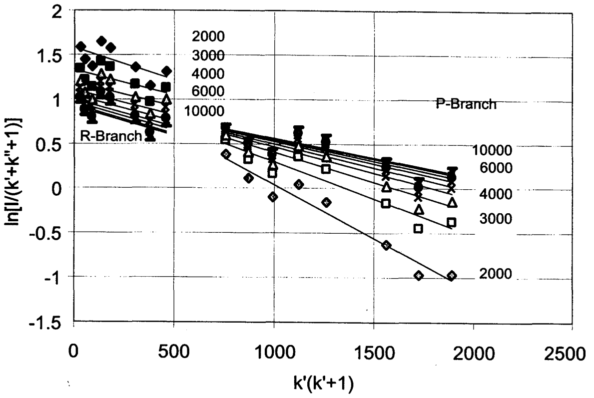

Fig. 4 Boltzmann plot of intensities inferred from allocating R and P branches of N_2^+ (0, 1) band.

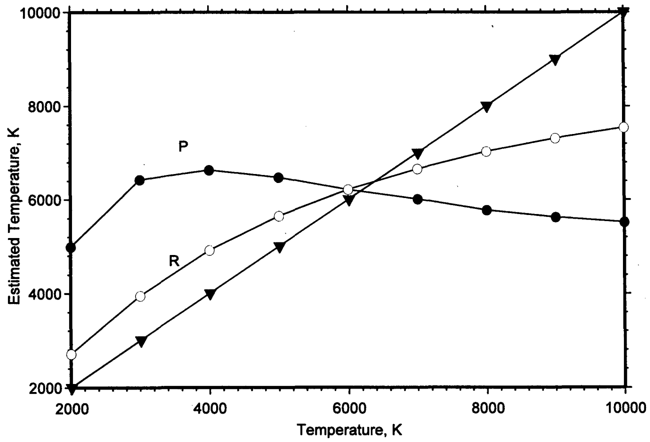

Fig. 5 Rotational temperature determination from N_2^+ (0, 1) band rotational peaks. Graphic solution of P- and R-branch allocation method for rotational temperature. Intersection of curves gives best estimate of T_r.

Method of Allocating P and R Branches for N_2^+ (B-X)

The method of allocating P and R branches involves calculating line intensity in the P and R branches of the (0, 1) transition in N_2^+. This previously unpublished method applies to band systems consisting of resolvable peaks of unresolved overlapping P and R branches.[6] The first step is to theoretically calculate spectra with a very high resolution so that well-resolved individual rotational lines are obtained at different temperatures; e.g., 1000 to 10,000 K in increments of, say, 500 K. The peak intensities of P- or R-branch rotational lines, I_P and I_R, respectively, are determined and tabulated. The second step is to generate theoretical spectra at a resolution comparable to the experimental spectra. These spectra consist of peaks associated with overlapping P- and R-branch lines. Overlapping pairs of rotational lines of P and R branches are noted and the theoretical ratios, $B = I_P/I_R$, are tabulated for each pair at different temperatures. This ratio, B, is used to allocate part of the measured peak intensity to each of the component branch rotational lines. Component intensities are then used to determine the temperatures (T_P and T_R) from the standard Boltzmann equation by plotting $\ell n(I_P)$ and $\ell n(I_R)$ vs 1/kT. Theoretical R- and P-branch component intensities are given by

$$I_{Rc} = I_{\exp}[1/(1 + B)] \quad (3)$$

$$I_{Pc} = I_{\exp}\{1/[1 + (1/B)]\} \quad (4)$$

where $I_{\exp}$ is the measured (experimental) combined intensity integrated over each peak of overlapping P- and R-branch components. Parametrically for each T_r, sets of component P and R intensities are plotted as Boltzmann plots (Fig. 4). The P- and R-branch temperatures, T_P and T_R, determined from the slopes are then plotted against the temperature assumed in the allocation (Fig. 5). The best estimate of rotational temperature is the one at which two branch temperature curves cross the theoretical curve. Ideally, curves should cross at the same temperature; but in some cases there may be two temperatures, and the correct temperature is picked by roughly comparing the peak of the P- and R-branch contours with the estimated temperatures.

The example (Fig. 5) shows an analysis of the (0, 1) band rotational spectrum. From this we see that two curves cross the $T = T_r$ line near 6000 K, which determines the rotational temperature of N_2^+. There is a difference of up to 400 K between crossing points. Errors in technique may result from overlapping more than one P- and one R-branch line, or misidentifying lines, inaccurate wavelength integration, and background effects. The Boltzmann plots indicate that because more than one P and R pair of lines associated with other quantum numbers overlaps, a relatively good straight line is available only for a limited number of rotational quantum numbers. The standard error of fit of eight points (Fig. 4) is 1200 K for the P branch and 2500 K for the R branch. The standard error of mean is estimated to be 1100 K for data in this figure. This estimated error is based on scatter seen in Boltzmann fits, including all sources of error. Individual errors cannot be determined.

Least-Squares Method for Intensity Integral Ratios in the N_2^+ B-X (0, 1) Spectrum (Léger Technique)

The third technique for rotation (Léger et al.[11]) uses a least-squares computation of differences between computed and experimental ratios of P-bandhead rotational lines and other overlapping P and R lines. For example, range 7 (Table 2) covers the bandhead for (0, 1) transitions consisting of P-branch transitions only, and the wavelength ranges 1–6 cover single overlapped P- and R-branch rotational lines. The set of ratios 1/7 to 6/7 may therefore be used in a least-squares computation. With I_i representing radiation intensity integrated over wavelength interval i, the experimental spectra would yield a set of ratios

$$R_{ie} = (I_i/I_7)_e \tag{5}$$

Likewise, the synthetic spectra (equilibrium) computed for a given $T_v = T_r$ yields

$$R_{ic}(T_r) = (I_i/I_7)_c \tag{6}$$

The Léger technique defines a function

$$F(T_r) = \frac{1}{N}\left\{\sum [R_{ie} - R_{ic}(T_r)]^2\right\}^{1/2} \tag{7}$$

where the sum would go to $N = 6$. The equilibrium temperature minimizing the function $F(T_r)$ is the rotational temperature sought. While individual ratios may be used to define a temperature by comparison with ratios computed as a function of temperature, this method gives something of an average for all lines used. Discrepancies may occur in individual rotational line intensities, but this method should be more accurate than a single ratio and should basically give a best fit for the rotational lines involved. This technique is applied to the same set of data as for previous methods involving the N_2^+ (0, 1) bandhead region. A minimization of $F(T_r)$ using three integral ratios yields $T_r = 6100$ K, whereas if we use six integral ratios the result is $T_r = 7000$ K. This implies that the ratios are not consistent, possibly because of background effects. A comparison of technique sensitivity for the two sets of intensity integral ratios is shown in Fig. 6, where $F(T_r)$ is plotted against T_r. We see that the set of three ratios has a deeper well than the set of six ratios, which is consistent with the sensitivity curves of Eq. (1) found in the ratio technique.

Table 2 Wavelengths for intensity integrals used for T_r determination for the (0, 1) bandhead region using the Léger technique[11]

Range no.	Integral ranges, nm λ_1	λ_2
1	427.00	427.20
2	426.79	426.92
3	426.53	426.70
4	426.26	426.42
5	424.52	424.75
6	424.91	425.13
7	427.55	428.00

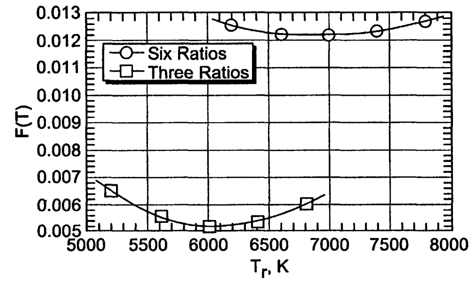

Fig. 6 Root mean square of difference in ratio of intensity integrals [Eq. (7)] for N_2^+ (0, 1) band as a function of T_r (Léger technique[11]).

Vibrational Temperature of N_2^+

Three techniques can be applied to the N_2^+ spectrum to determine vibrational temperature; these are described here, including ones not possible for N_2. The first two involve correlating theoretical intensity ratios of bandheads with vibrational temperature, then obtaining ratios of measured bandhead intensities. In the first case, only peak values are taken; in the second case, integrals over small wavelength ranges centered on the peak are used. We only discuss the second of these cases. The third technique involves fitting individual basis spectra associated with each upper vibrational energy level with measured spectra. The measured spectrum used in these analyses is given in Fig. 7.

Ratios of Bandhead Intensity Integrals

This technique, similar to the one for determining T_r for N_2^+, obtains ratios of integrals of intensities of vibrational bandheads and infers temperature from calculated ratios of integrals of computed spectra; e.g., codes NEQAIR,[12] NEQAIR5, and NEQAIR2.[13] Although peak bandhead intensities were used to determine the vibrational temperature,[10,11,14–16] it is our opinion that integrals of intensities over the bandheads should be used to avoid questions of adequate resolution and line broadening. Ratios of intensities correspond to ratios of various vibrational transitions; e.g., (v', v'') or (0, 1) to (2, 3), etc. Intensities for each transition were integrated over the wavelength ranges given in Table 3. The ratios of integrated intensities for each bandhead pair were correlated with T_v; in cases where there is a dependence on T_r, the vibrational temperature was inferred from the correlation corresponding to the best estimate of T_r. A measure of the background was subtracted from each integral. Background in a given region is estimated by curve fitting the adjacent region not covered by a band of interest (toward a longer wavelength). The background under this band of in-

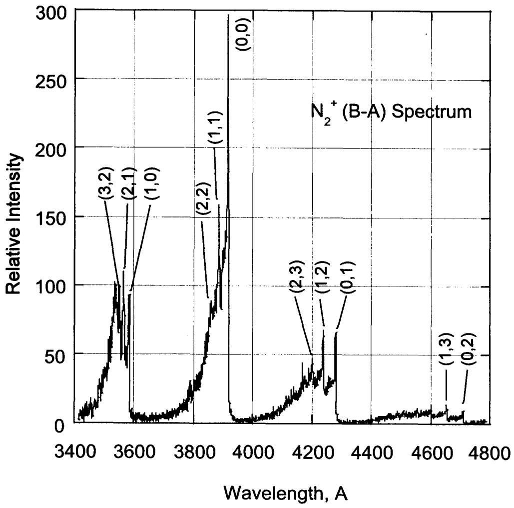

Fig. 7 Measured N_2^+ (B-A) spectrum annotated with identification of (v', v'') bandheads. Distance from surface is 2.54 cm.

Table 3 Wavelengths for intensity integrals used for T_v determination for the N_2^+ bandheads region using the ratio technique

Bandhead	Integral ranges, nm	
v', v''	λ_1	λ_2
2, 0	470.6	471.2
3, 1	465.0	465.4
1, 0	427.6	428.1
2, 1	423.5	423.9
3, 2	419.7	420.2
0, 0	391.2	391.7
1, 1	388.2	388.6
0, 1	358.0	358.4
1, 2	356.2	356.6
2, 3	354.6	355.1

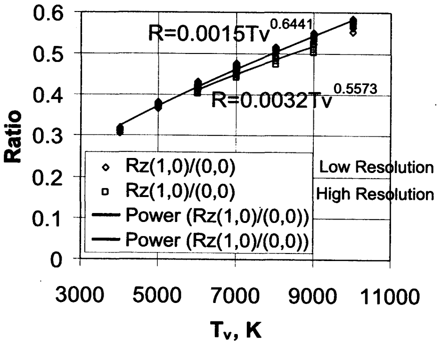

Fig. 8 Ratio of intensity integrals (1, 0)/(0, 0) bandheads for low- and high-resolution data. Background is subtracted. Sensitivity factors are shown from curve fits to power function.

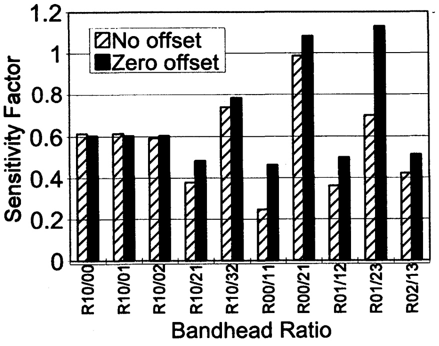

Fig. 9 Sensitivity factors for ratios of bandheads for N_2^+ (B-X) transition calculated from 0.0232-nm bandwidth calculations. Background subtracted is denoted zero offset.

terest is obtained by extrapolating the curve fit to the range of integration. Results for bandhead ratios (1, 0)/(0, 0) are given in Fig. 8 for two sets of measured spectra obtained at different resolutions (~0.08 and 0.28 nm). Note that the higher-resolution case yields somewhat more sensitive results. Sensitivity factors (Fig. 9), which were derived from curves such as these, are consistent with the fact that higher sensitivity is associated with greater differences in upper energy levels associated with integrated intensities. In many cases we can see that there is greater sensitivity when the background corresponding to the rotational lines is subtracted before the ratios are computed.

Curve Fits of Vibrational-Level Basis Spectra

The second technique[17] (also used for N_2) is to fit measured intensities to N_2^+ (B-X) v'-basis sets to obtain relative populations of the v' states. The slope of the Boltzmann plot for these populations yields T_v. To use this technique T_r must first be determined because the basis sets depend on it. The measured spectrum in the wavelength range 320–478 nm is fit to the basis spectra to determine the relative population of the v' levels. A Boltzmann plot of these populations (Fig. 10) yields the vibrational temperature. Only the lower five states are useful, however, because of overlapping basis spectra and possible nonequilibrium effects. With this overlapping, it becomes crucial to ensure the wavelengths match precisely. Overlap is greater for higher vibrational states, particularly in the wavelength ranges 345–355 nm and 320–330 nm.

Vibrational Temperature of N_2

Determination of vibrational temperatures for N_2 may be categorized by two techniques. The first compares intensity integrals over wavelength in various parts of the spectrum; the second is based on curve fits of measured spectra to computed basis spectra. Each basis spectrum corresponds to the upper v' state of a molecular electronic transition.[17]

Ratios of Integrated Intensities

The first technique included here estimates the N_2 vibrational temperature; it was described by Blackwell et al.,[1] who measured the broad Δv spectra regions of the N_2 transition $B^3\Pi_g - A^3\Sigma_u$ (first positive) in the wavelength range 563–766 nm. Measured integrated intensity ratios were compared with ratios of integrated intensities calculated using the NEQAIR code.[12] A measured spectrum is shown in Fig. 11, along with the wavelength ranges for I_2, I_3, and I_4. Integrated intensity ratios of three Δv regions (Fig. 11) are given in Fig. 12 as functions of T_v for $T_v = T_r$ and $T_v = T_r + 8000$ K. Rotational temperature differences as large as 8000 K contribute an error of only 1000 K in vibrational temperatures, provided the spectra contain only first positive (B-A) radiation. Sensitivity factors, defined earlier as the logarithmic derivative of the inten-

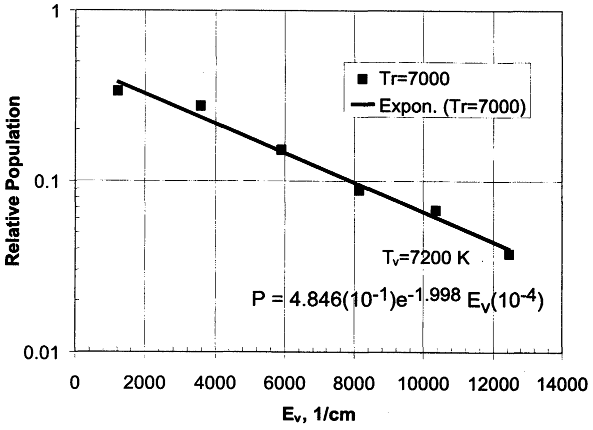

Fig. 10 Boltzmann plot of N_2^+ vibrational population distribution. The inferred vibrational temperature is 7200 K. Measurements are at 2.54 cm with T_r = 7000 K.

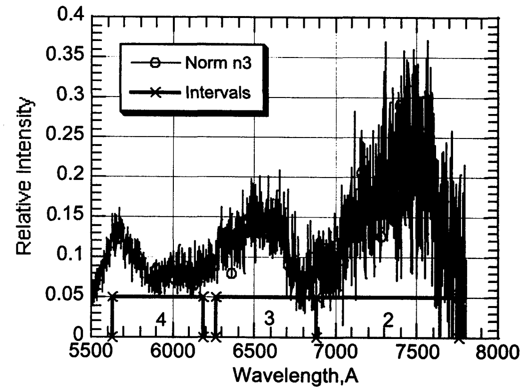

Fig. 11 Measured intensity in region of N_2 (B-A) spectrum 2.54 cm from surface in shock layer showing intensity integral intervals.

Table 4 Wavelength intervals, intensity integral definitions, and ratio designations for ratio technique for N_2 (B-A) spectra

Integral no.	Δv	Wavelength range, nm	Ratio designations and sensitivity factors			
			R_i	f_{ij}	R_{ij}	f_{ij}
I_2	2	688.0–776.0	$R_2 = I_2/(I_2 + I_3 + I_4)$	0.69	$R_{78} = I_7/I_8$	0.93
I_3	3	626.0–688.0	$R_3 = I_3/(I_2 + I_3 + I_4)$	0.45	$R_{68} = I_6/I_8$	2.17
I_4	4	563.3–619.0	$R_4 = I_4/(I_2 + I_3 + I_4)$	1.48	$R_{58} = I_5/I_8$	3.48
I_5	5	500.0–550.0	—	—	—	—
I_6	4	550.0–600.0	—	—	—	—
I_7	3	600.0–690.0	—	—	—	—
I_8	2	690.0–760.0	—	—	—	—

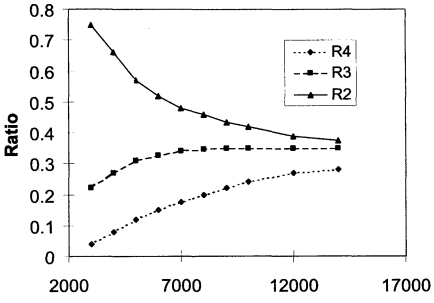

Fig. 12 Ratio of intensity integrals for N_2 (B-A) peaks from Ref. 1.

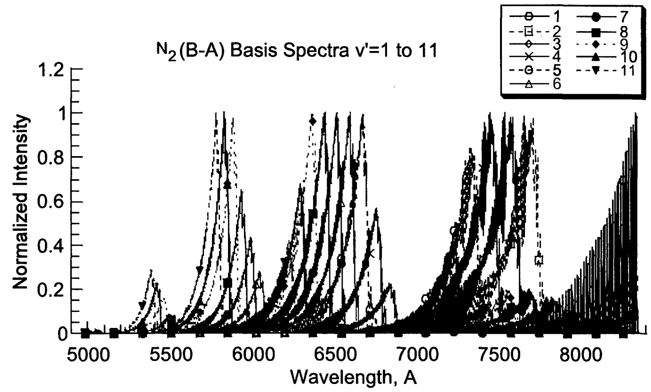

Fig. 13 Normalized basis spectra for N_2 (B-A) spectrum used for least-squares determination of populations of vibrational levels of N_2 B-state. T_r = 6000 K.

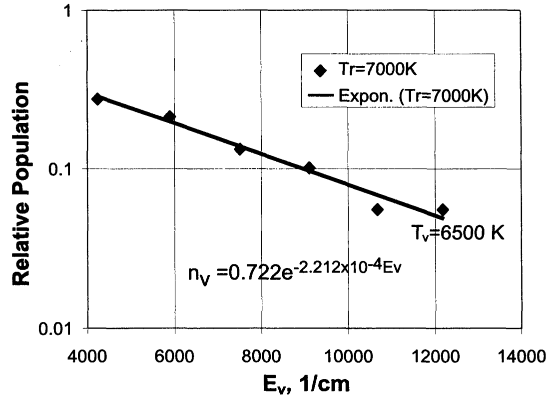

Fig. 14 Boltzmann plots of N_2 vibrational population distribution. Measurements at 2.54 cm with T_r = 7000 K. The inferred vibrational temperature is 6500 K.

sity ratio to the temperature, can also show this trend because the absolute value of sensitivity factors decreases as temperature increases. This means the integral intensity ratio technique is not very accurate at high temperatures. Recently, the ranges were refined and augmented to include other Δv regions (i.e., I_6, I_7, and I_8). Ratios were formed by these pairs of integrals. As shown in Table 4, R_{68} and R_{58} have greater sensitivity factors than R_2, R_3, and R_4.

The set of wavelength intervals in Table 4 has not been optimized. However, it may be possible to increase the sensitivity by considering other wavelength ranges and different ratios.

Curve Fits of Vibrational Basis Spectra

The second technique to determine T_v for N_2 is to fit the measured spectra to theoretically computed basis sets corresponding to transitions from different upper v' states of N_2 (B-A) (Fig. 13). Each basis spectrum shown is normalized to peak intensity. The relative populations of v' states are then found by curve fits of measured spectra to the basis sets for $v' = 1$ to n; an account is made for the transition probability of each v' transition. Relative populations can then be plotted on a Boltzmann plot to determine vibrational temperature (Fig. 14). This technique is particularly useful for determining populations of lower-lying states. As seen in Ref. 8 it may be necessary to include basis sets for any overlapping spectra, such as those from the N_2^+ Meinel system (A-X).

Combination Method for T_r from N_2 (B-A) Spectra

It is difficult to determine T_r from N_2 (B-A) spectra because of the very poor resolution of rotational lines. An estimate of T_r may be determined by using the following method.

Method of Minimum Least-Squares Deviation from Calculated Spectra

1) This technique, based on least-squares fits of measured spectra to calculated spectra,[17] is similar to the method of determining T_v. Basis spectra for N_2 (B-A) vibrational transitions are calculated for a set of T_r. These computed basis spectra are fit to the measured spectrum using the fitting procedure described earlier from which the population of vibrational states over a range of v' is determined. The fitting code computes the rms deviation of the fitted spectrum to the measured spectrum. The most probable rotational temperature is attributed to the temperature at which the rms deviation is at a minimum. However, sensitivity is not very good because the minimum is very shallow, and it is difficult to assess the accuracy quantitatively. Wavelength uncertainties affect this technique's accuracy. For low resolution, this is less a problem; but the technique does not discriminate well between rotation and vibration.

2) A similar technique can be used to parametrically vary T_v. A single basis spectrum is generated that combines all v' basis spectra for a given population distribution of vibrational states. A Boltzmann distribution corresponding to T_v is assumed, and a parametric set of basis spectra for a range of T_r and T_v is generated. The rms deviation between measured and calculated spectra is determined for each T_r and T_v pair. The combination at which the rms deviation is at a minimum determines temperature. As in Fig. 15, this result is T_r = 6880 K and T_v = 10,000 K. If one suspects the populations of vibrational states are non-Boltzmann, the spectra can then be refit assuming T_r as determined earlier, thus obtaining a population

Table 5 Temperatures determined from analysis of spectral measurements using various techniques[a]

Species	Technique	T_r, K	Error, K
	Rotational temperature		
N_2^+	Mean of ratios of intensity integrals	6,000	1,100
N_2^+	Allocation of P and R	6,100	1,100
N_2^+	Léger technique	6,100	900
N_2^+	Mean	6,100	600
N_2	Minimization of rms deviation	7,500	1,000
N_2	RMS minimum for T_r and T_v	6,900	700
N_2	Mean	7,100	600
N_2 and N_2^+	Mean of N_2 and N_2^+	6,600	400
	Vibrational temperature		
N_2^+	Mean of ratios of intensity integrals (three evaluations)	6,100	360
N_2^+	Mean of ratio of peak intensities	6,600	800
N_2^+	Curve fit of basis spectra (four evaluations)	7,300	800
N_2^+	Mean	6,300	300
N_2	Ratio to integral sum	8,500	800
N_2	Ratio of intensity integrals	6,800	400
N_2	Curve fit of basis spectra	7,200	1,000
N_2	RMS minimum for T_r and T_v	10,000	1,000
N_2	Mean	7,400	300

[a] Distance 2.54 cm from surface of model in shock layer.

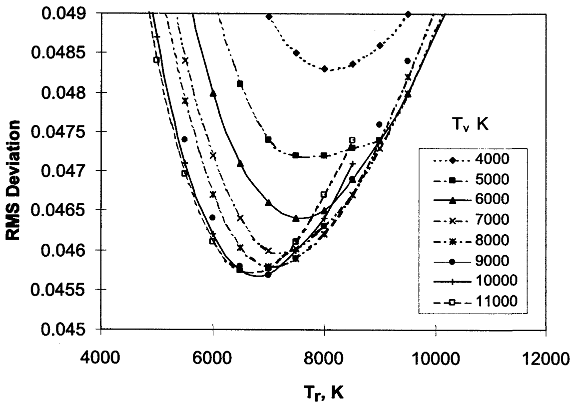

Fig. 15 Root mean square deviation of a measured N_2^+ (B-X) spectrum from calculated spectra with T_r and T_v as parameters. The minimum represents an estimate of best-fit temperatures; T_r = 6800 K and T_v = 10,000 K.

distribution of vibrational states. Although very crude, these are the only techniques available for estimating the rotational temperature of the N_2 (B-A) transition without extremely high-resolution measurement. This suffers from the problem that low-resolution spectra can be similarly affected by T_r and T_v; that is, a portion of the spectrum may increase with T_r or T_v relative to another portion of the spectrum. This increases one temperature while decreasing the other temperature. Also, one should be judicious in selecting the wavelength range over which to curve fit to avoid overlapping spectra from other species or transitions. This is particularly true with long wavelengths that have overlapping N_2^+ (A-X) emissions.

Results and Examples

The techniques described earlier were applied to measurements of the emission spectra in the shock layer of a blunt body in arcjet flow.[3] The mass flow rate of the gas was 0.0544 kg/s; the bulk enthalpy of the flow was 8.72 MJ/kg, and the centerline enthalpy was about 2–3 times the average.[18] Flow expanded from the arc heater through a conical nozzle with a 15-deg half-angle expansion to approximately Mach 5. Flow then impinged on the blunt body, which generated a shock wave and shock layer. Stagnation point pressure on the model was about 1300 Pa. Because of its high enthalpy, the flow was partially dissociated and slightly ionized. We expect that the freestream was far from thermal and chemical equilibrium caused by low pressure and high velocity. The spectra were measured with a spectrometer that had two general-resolution setups. One spectrometer had a relatively high resolution of 0.0232 nm, and the other spectrometer had a relatively low resolution of 0.0692 nm.[1–6] In neither case were the rotational lines completely resolved. It was therefore necessary to determine rotational temperature from an integral or envelope, or by using fitting techniques. The vibrational temperature is estimated for N_2 and N_2^+ separately because it is not known whether a vibrational interchange between these species is sufficiently fast for them to be in equilibrium with each other.

Temperatures in this paper are determined from spectra measured 2.54 cm from the surface of the model. The measured spectra analyzed here are shown in Figs. 2, 7, and 11. As can be seen in the single-temperature viscous shock-layer calculation,[4] the flow at that point is in the inviscid portion of the shock layer. Methods described in the previous section were applied to the measurements, and the resulting temperatures are summarized in Table 5. An attempt to ascribe an uncertainty to those measurements is included, as well as averages and their associated standard error. It can be seen that results differed considerably, depending on which technique was used. Using several techniques and measurements naturally improves confidence in the averages. Mean temperatures determined from the various techniques, as well as mean temperatures based on both N_2 and N_2^+, are shown in Table 5. The means and standard error (Table 5) are weighted by each other. Each value is assumed to be an independent experiment with its own error. The means are calculated using standard error-analysis techniques.[19] Mean temperature is then determined from

$$T_{\text{mean}} = \frac{(T_n/S_n^2 + T_m/S_m^2 + \cdots + T_N/S_N^2)}{S_n^{-2} + S_m^{-2} + \cdots + S_N^{-2}} \tag{8}$$

and its corresponding standard error is

$$\frac{1}{S_{n,m,\ldots,N}^2} = \frac{1}{S_n^2} + \frac{1}{S_m^2} + \cdots + \frac{1}{S_N^2} \tag{9}$$

where S_k is the standard error and T_k is the mean of k measurement of T, respectively.

Discussion and Conclusions

Various means of determining vibrational and rotational temperatures of N_2 and N_2^+ have been applied to measure spectral radiation in the shock layer of an arcjet flow impinging on a blunt model. These methods use computed spectra and, therefore, are somewhat dependent on the accuracy of spectroscopic constants used in these calculations. This paper does not address the accuracy of computed spectra, except to obtain good matching of spectra features with wavelengths. These techniques assume thermal equilibrium (Boltzmann population) of each spectral system. However, it is not assumed that the temperatures of all the systems are the same. Another implicit assumption is that there is negligible overlap of one system with another. At least the overlap is avoided by judiciously selecting wavelength ranges for fits and integral ratios. Further discussion of techniques to deal with overlap is given in a companion article.[8] The spectral fitting technique can deal with overlapping systems, and even give some indication of the relative population of different molecules or electronically excited states.

The techniques applied here have been used by us and others to determine rotational and vibrational temperatures. This paper summarizes these techniques and presents some measure of their accuracy, indicating which are more sensitive to temperature. Most of the techniques presented permit the determination of rotational and vibrational temperatures separately, although often one depends on the value of the other. There are regions of the spectrum of N_2^+ that are relatively insensitive to either T_r or T_v, but not to both. These give the most reliable results for one without influencing the uncertainty of the other. In particular, the structure of the (0, 1) bandhead region depends almost entirely on T_r and is not influenced by T_v. Similarly, the bandhead ratios for the (1, 0), (0, 1), (0, 0), and (0, 2) regions are fairly insensitive to T_r, particularly when the background is subtracted; yet it is best to determine T_r first when using intensity ratio techniques to find T_v. All techniques assume that temperature is defined by a Boltzmann population of states, usually the lowest few states. Spectroscopic determination of the population of higher vibrational states is difficult because of overlapping bands and the influence of the overlapping rotational spectra of lower states on the bandheads of higher vibrational states.

Relative intensities of different parts of the spectrum can be used to measure temperature. These features can be correlated with the temperature in a global least-squares fit to the measured spectrum. A more accurate variation of this technique fits basis spectra that depend only on the vibrational level to the measured spectrum. Other techniques are based on correlations of ratios of integrals of one part of the spectrum to another. Depending on which features or wavelengths are used, the chosen technique may be more or less sensitive to the ratio. We have presented sensitivity factors that are consistent with the general principle that the greater the difference between upper energy levels the greater the sensitivity, and the more accurately we can determine the temperature. Because background radiation from a continuum may be present, it is useful to be able to subtract background from molecular radiation. Also, sometimes the underlying rotational structure may be subtracted to enhance the accuracy of the vibrational temperature determination.

Many techniques may be used and the results averaged. Because some techniques are more accurate or sensitive than others, we can weight the averages by sensitivity factors or estimates of the standard error of each measurement. The overall standard error based on all methods is about 4% for T_v and about 10% for T_r. However, errors for T_r (Table 5) using the N_2^+ and N_2 spectra indicate there is a large difference in results from the two molecules than in the error of each. It is therefore tempting to say that the rotational temperatures of the two molecules differ; but, based on the collision number in the flow, this is probably not the case. It is likelier that the error is really in the neighborhood of 1000 K, or 16%. Whether there is a large difference in the vibrational temperatures of N_2 and N_2^+ is questionable. It seems unlikely if the flow is close to thermal equilibrium. If the formation of molecular species is rate controlled (nonequilibrium), however, these molecules may be formed preferentially in higher vibrational and rotational energy levels. This might result in a higher temperature for N_2. An investigation of the rates of formation would be necessary to resolve this issue because it is difficult to directly measure populations of higher energy states. It is thus possible that the arcjet flow may not be in thermal equilibrium; therefore, it is useful to determine T_r and T_v independently. The accuracy of determination affects our ability to discriminate and say whether these temperatures are equal; i.e., whether the flow is in thermal equilibrium or nonequilibrium.

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