J. Astron. Space Sci., Vol.6, No.2, 75-89(1989)

# DETERMINATION OF VIBRATIONAL POPULATION DISTRIBUTION FOR THE $N_2^+$(1N) ION BAND SYSTEM FROM SPACELAB 1

**Jong Won Eun**
Satellite Communications Section, Electronics and Telecommunications Research Institute
(Received September 5, 1989; Accepted October 20, 1989)

## Abstract

The Spacelab 1 data represented the first multiband spectral measurements of the $N_2^+$ first negative ion bands system in the thermospheric dayglow, and the first opportunity to make a detailed comparison of the vibrational and rotational distributions over bands out to $v'=5$. The main purpose of this study was to deduce the excitation processes of $N_2^+$(1N) bands by determining vibrational population distributions for the upper states of $N_2^+$(1N). The vibrational population distributions to achieve a best fit to the measured Spacelab 1 data were summarized and also compared with those theoretically derived.

## I. Introduction

The $N_2^+$ first negative system results from the $B^2\Sigma_u^+ - x^2\Sigma_g^+$ transitions. A simplified energy level diagram is shown in Figure 1. Emissions from this system were the first seen in the twilight(Slipher, 1933) and excitation mechanisms for the $B^2\Sigma$ state of $N_2^+$ were proposed shortly thereafter. Saha(1937) suggested photoionization and electron impact ionization excitation;

$$N_2(X^2\Sigma_g^+) + h\nu\,(\lambda < 661\,\text{Å}) \rightarrow N_2^+(B^2\Sigma_u^+) + e \quad \cdots\cdots (1.1)$$

$$N_2(X^2\Sigma_g^+) + e^*(E > 18.7\text{eV}) \rightarrow N_2^+(B^2\Sigma_u^+) + 2e \quad \cdots\cdots (1.2)$$

while Wulf and Deming(1938) proposed resonance scattering of sunlight by the $N_2^+$ ion;

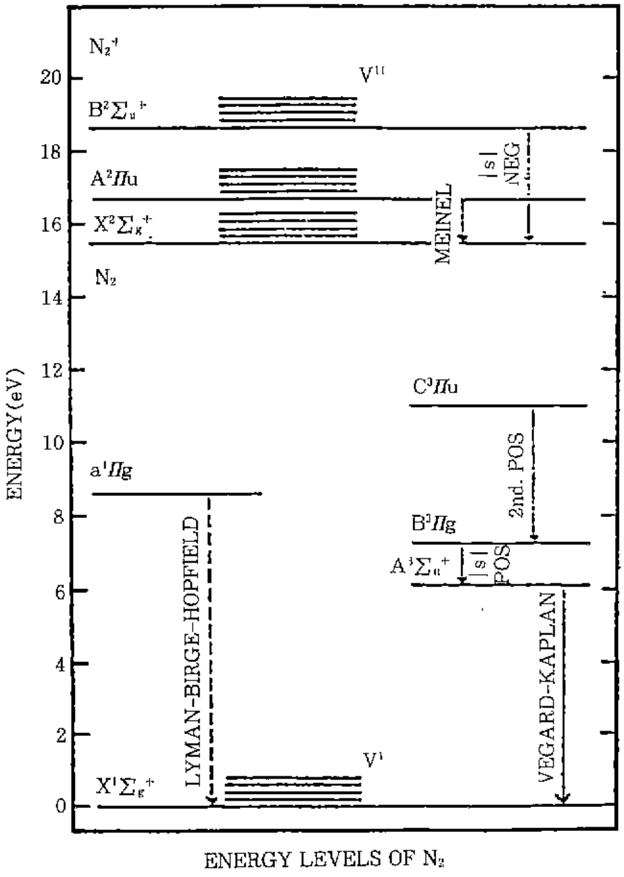

**Fig. 1** A simplified energy level diagram of $N_2$ and $N_2^+$ (Orsini, 1977).

$$N_2(X^2\Sigma_g^+)+hv \rightarrow N_2^+(B^2\Sigma_u^+) \quad \cdots\cdots \quad (1.3)$$

Stormer(1939) pointed out that the spectra of sunlit auroral rays at altitudes between 400 and 650 km showed unusually great development of the vibrational sequences.

A theoretical study by Bates(1949b) concluded that in the dayglow, the dominant process would be resonance fluorescence. In a comprehensive study of the available $N_2^+$ first negative spectral observations, Bates(1949a), again working with sunlit auroras, concluded that resonance fluorescence of $N_2^+$ ions was the major process. Furthermore, Bates(1949a) found the ratio of v' =0, 1 and 2 to be 1:0.40:0.27 for this mechanism, indicating that the vibrational temperature of the $N_2^+$ was in resonance with sunlight at 4500°K.

In the same year Swings(1949) proposed that the rotational line intensities would be modified by thd Fraunhofer lines of the solar spectrum, thus allowing a distinction to be made between a "thermal" type distribution and that resulting from fluorescence. A study of high altitude sunlit auroral rays by Vallance Jones and Hunten(1960) at 4 Å spectral resolution found the vibrational and rotational temperatures to be in equilibrium with an atmosphere at 2200°K. They concluded that the loss rate for $N_2^+$ ions is fast enough to prevent the ions from reaching radiative equilibrium. Subsequent measurements in the midlatitude twilight of the $N_2^+$ first negative 0-0 band at 3914Å by Broadfoot and Hunten(1966), found a lower rotational temperature of 1600°K.

The Spacelab 1 data represent the first multiband spectral measurements of the $N_2^+$ first negative system in the dayglow, and thus the first opportunity to make a detailed comparison of the vibrational and rotational distributions over bands out to $v'=5$. and free of potential complications such as scattering in the lower atmosphere or the particle impact effects associated with sunlit auroral rays.

The primary excitation mechanism for the $N_2^+$ first negative bands, in addition to direct photoionization, is resonance fluorescence scattering(Bates 1949a, 1949b; Torr and Torr 1982; Fox and Dalgarno 1985) of solar near UV radiation:

$$N_2(X^2\Sigma_g^+) + h\nu \rightarrow N_2^+(B^2\Sigma_u^+) \rightarrow N_2^+(X^2\Sigma_g^+) + h\nu \cdots\cdots\cdots\cdots \quad (1.4)$$

Following pumping of the X to the B(and A) states by absorption of solar radiation, the spontaneous decay of these states acts as a source of vibrational excitation for the ground state ions. In the absence of loss processes, the resulting $N_2^+$ vibrational distribution would be Boltzmann, in radiative equilibrium with the sunlight characterized by a temperature of 4500°K and lowered to ~2000°K by the Swings effect. This places an upper limit on the vibrational populations generated by resonance fluorescence scattering. Quenching will act to lower the effective temperature of the distribution.

The photochemistry of $N_2^+$ in the ionosphere has been extensively discussed in the literature in recent years(Oppenheimer *et al.* 1976; Breig *et al.* 1983; Abdou *et al.* 1984; Fox and Dalgarno 1985).

There are two main sources of $N_2^+$ ions in the daytime ionosphere:

EUN

1. Photoionization by solar EUV radiation

$$N_2+hv \xrightarrow{J_1} N_2^+(X)+e \quad \cdots\cdots \tag{1.5}$$

where $J_1$ is the photoionization frequency(Torr and Torr 1985), and

2. The charge exchange process

$$O^+(^2D)+N_2 \xrightarrow{k_1} N_2^++O \quad \cdots\cdots \tag{1.6}$$

where $k_1=8\times10^{-10}$(Rowe *et al.* 1980; Johnsen and Biondi 1980). The main loss processes are:

The main loss processes are:

1. Dissociative recombination

$$N_2^++e \xrightarrow{\alpha_1} N+N \quad \cdots\cdots \tag{1.7}$$

where $\alpha_1$ is the dissociative recombination coefficient and

2. Ion-molecule interchange

$$N_2^++O \xrightarrow{k_2} NO+N \quad \cdots\cdots \tag{1.8}$$

where $k_2=1.4\times10^{-10}(T_i/300)$(McFarland 1974: Torr 1979).

The validity of the above photochemical scheme has been the subject of much debate over the past half decade because it over-estimates the concentration of $N_2^+$ in the ionospheric F region above~220km. A number of solutions have been proposed which are relevant to the interpretation of the Spacelab 1 $N_2^-$ observations reported here.

In order to increase the destruction of $N_2^+$, Torr and Torr(1980 1982) and Abdou *et al.*(1982, 1984) suggested that reaction(1.6) could produce $N_2^+$ ions in vibrational levels $v'>0$ in the ground electronic state, which might enhance the rate of the reverse reactions;

$$N_2^+(X)(v'>0)+O \rightarrow O^+(^4S, ^2D)+N_2 \quad \cdots\cdots \tag{1.9}$$

leading to enhanced $N_2^+$ removal.

Abdou *et al.*(1982, 1984) specifically suggested that if $N_2^+$ is produced in(or near) the v′=5 level of the X state, reaction(1. 9) is accidentally energetically resonant if the product is $O^+(^2D)$.

It should be noted that Orsini *et al.*(1977) and Abdou *et al.*(1984), pointed out that if the ionospheric $N_2^+$ recombination rate $\alpha_1$ is about a factor of 2 larger than the value derived from laboratory measurements, the problem of excess $N_2^+$ ions can be largely resolved. In their treatment of $N_2^+$ ion chemistry, Fox and Dalgarno(1985) adopted the larger value for $\alpha_1$. Fox and Dalgarno also pointed out that measurements of the $N_2^+$ first negative bands could decide whether there is any evidence of anomalous vibrational excitation produced by the precursor reaction(1. 6). The absence of such excitation would eliminate the schemes proposed by Torr and Torr(1980) and Abdou *et al.*(1984).

The ISO data therefore provide a unique opportunity to test an important step required by both the above mentioned models.

## II. Observation from Spacelab 1 of Space Shuttle Mission

The Spacelab 1 mission was launched on November 28, 1983 into a 57° inclination orbit and continued for ten days. The primary purpose of the mission was to test the Shuttle/Spacelab combination and the interfaces provided by these systems with a varied complement of instruments and investigation objectives. As might be expected for such a complex mission, science objectives were compromised by several factors: the planned-for second TDRS satellite was not launched and the single TDRS satellite that was in orbit was not in the correct location and did have problems. All of this resulted in significantly less real time coverage than had been earlier anticipated, and to acquisition difficulties at times. In addition, problems were encountered with the interface(RAU 21) through which the NASA pallet mounted instruments were operated, resulting in considerable loss of observation opportunities. Additional problems included the failure of the High Data Rate Recorder(HDRR) which resulted in the loss of key data. Further, the ISO was significantly impacted by an interference problem between the HDRR and the High Rate Multiplexer(HRM) when the latter was the operated in a particular format channel. This latter problem caused numerous sync losses and "noise spikes" to be inserted in the data stream. Also the launch slips that the mission experienced led to a launch time that placed the vehicle into an orbit close to the terminator, rather than the planned noon-midnight orbit. Thus the data set is biased towards high solar zenith angles.

The above problems together with the test flight of a complex vehicle and payload led to a less-than-optimized scientific data product for the ISO. Nonetheless, it was possible to obtain at least samples of each of the principal data sets that were the ISO Spacelab 1 objectives.

In this study we shall address only those data segments that were acquired with the field of view looking into the high altitude dayglow; the observations that were made looking horizontally from the vehicle at its orbit altitude of 250km, or looking at angles above the horizontal. The data sets obtained with the instrument looking into the vehicle wake(i. e., back along the orbit track) which are called as wake data were obtained on the first day of the mission are summarized in Figure 2.

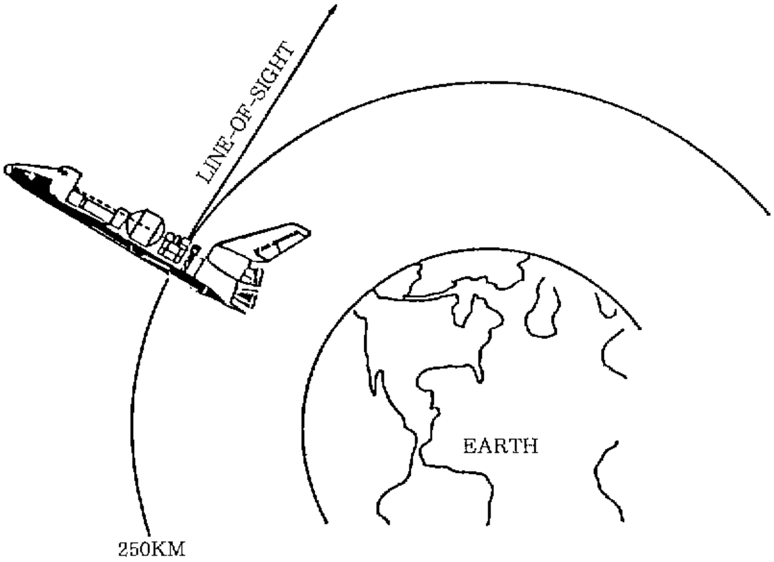

**Fig. 2.** Viewing geometry for 250km tangent ray height observations of wake data.

## Ⅲ. Results

### 1. Theoretical Determination of Vibrational Populations for $N_2^+$(1N)

We are going to theoretically determine the vibrational populations for $N_2^+$(1N) in much detail. The($X^1\Sigma_g^+$) electronic state is the ground state of the $N_2$ molecule(see Figure 1). Vibrational exchange takes place when two $N_2$ molecules collide, thus, driving the distribution towards a Boltzmann distribution(Walker, 1973). Therefore, if the vibrational distribution of ($X^1\Sigma_g^+$) is assumed to have a Boltzmann distribution, then, the number of molecules in the higher vibrational levels referred to the total number of molecules in the $X^1\Sigma$ state is given by

$$N_v=\frac{N}{Z}\exp(-G_0(v)/.6952T_{vib}) \quad \cdots\cdots (3.1)$$

where

$T_{vib}$=vibrational temperature in °K of $N_2(X^2\Sigma_g^+)$
$0.6952=k/hc$ in$(°K-cm)^{-1}$

where

k is the Boltzmann's constant in erg$(°K)^{-1}$
h is the Planck's constant in erg sec
c is the speed of light in cm $sec^{-1}$
$G_0(v)$ is the wave number in $cm^{-1}$ as a function of vibrational level(v), the subscript zero denotes that the energy levels are referred to the lowest level as zero.
z is the partition function and is given by

$$Z=1+\exp(-G_0(v=1)/.6952T_{vib})+\exp(-G_0(v=2)/.6952T_{vib})+ \quad \cdots\cdots (3.2)$$

where

$$G_0(v)=W_0v-W_0X_0v+W_0Y_0v \quad \cdots\cdots (3.3)$$

and

$$W_0 = W_e - W_eX_e + \frac{3}{4}W_eY_e$$

$$W_0X_0 = W_eX_e - \frac{3}{2}W_eY_e \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (3.4)$$

$$W_0Y_0 = W_eY_e$$

v is the vibrational quantum number

$W_e$, $X_e$ and $Y_e$ are vibrational constants and the subscript e implies equilibrium conditions of the anharmonic oscillator.

From Herzberg(1950)

$W_e = 2369.61$, $\quad W_eX_e = 14.456$, $\quad W_eY_e = +0.00751$

therefore, considering only the first five vibrational levels(0 to 4)

$G_0(v=0)=0.0$, $\quad G_0(v=1)=2345.2$, $\quad G_0(v=2)=4632.6$,
$G_0(v=3)=6905.5$, $\quad G_0(v=4)=9150.0$

Defining $\alpha(v) \equiv G_0(v=0)/.6952$

$\alpha(0)=0.0$, $\quad \alpha(1)=3373.4$, $\quad \alpha(2)=6663.7$,
$\alpha(3)=9933.7$, $\quad \alpha(4)=13161.7$

Notice that at least for the first five vibrational levels $\alpha(v)$ can be approximated to be $v\alpha(1)$ and let $\alpha(1)=\alpha$. So that for

| $v=0$ | $v\alpha=0.0$ | % error |
|---|---|---|
| $v=1$ | $v\alpha=3373.4$ | 0.0 |
| $v=2$ | $v\alpha=6746.8$ | 1.3 |
| $v=3$ | $v\alpha=10120.2$ | 1.9 |
| $v=4$ | $v\alpha=13493.6$ | 2.5 |

……………………………………………… (3.5)

If one tollerates a maximum 2.5% error in $v=4$ level, equation (3. 1) becomes

$$N_v=\frac{N}{2}\exp(-v\alpha/T_{vib})$$

equation (3. 2) becomes

$$Z=\sum_{v=0}^{\alpha}\exp(-v\alpha/T_{vib})$$

which is an exponential series and can be written as

$$Z=[1-\exp(-\alpha/T_{vib})]^{-1}$$

$$N_v=N\exp(-v\alpha/T_{vib})(1-\exp(-\alpha/T_{vib})) \quad \cdots\cdots (3.6)$$

By using parameters shown in (3. 5) and equation (3. 6), we can calculate $\frac{N_v}{N}$ and determine the relative vibrational populations with respect to different vibrational temperature, 2000°K, 4000°K, and 8000°K, respectively(see Table 1).

**Table 1.** Vibrational population distributions obtained from theory

| $v'\backslash T_{vib}$(°K) | 2000 | 4000 | 8000 |
|---|---|---|---|
| 0 | 1.0 | 1.0 | 1.0 |
| 1 | 0.15 | 0.24 | 0.23 |
| 2 | 0.028 | 0.106 | 0.148 |
| 3 | 0.005 | 0.045 | 0.097 |

## 2. Observational Determination of Vibrational Populations for $N_2^+$(1N)

In this section we shall discuss the $N_2^+$(1N) bands in greater detail using the wake observational data.

Figure 3 shows the major bands of the $N_2^+$ system from the wake data compared with a synthetic spectrum in which the resonance fluorescence is simulated by using a vibrational temperature of 2000°K. A rotational temperature of 900°K was used. The wake data are not well reproduced by this model which represents the vibrational distribution anticipated by the work

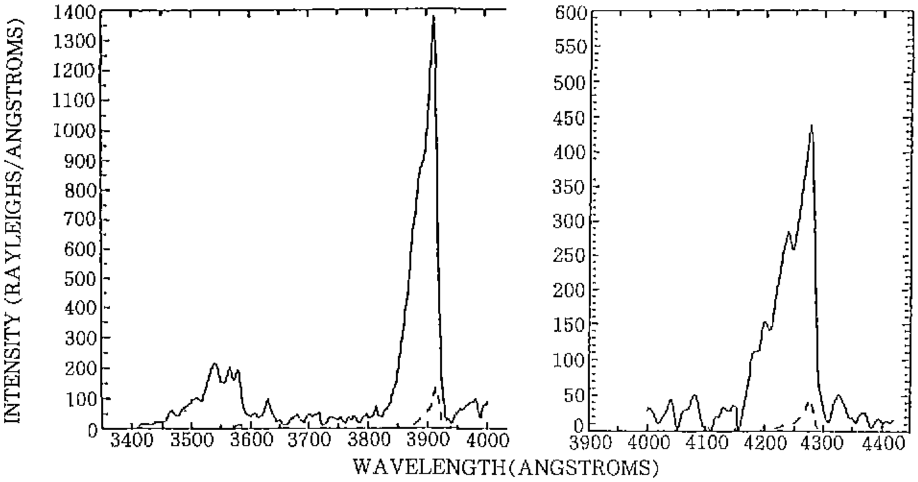

**Fig. 3** Major bands of $N_2^+$ first negative system as measured looking into the wake.

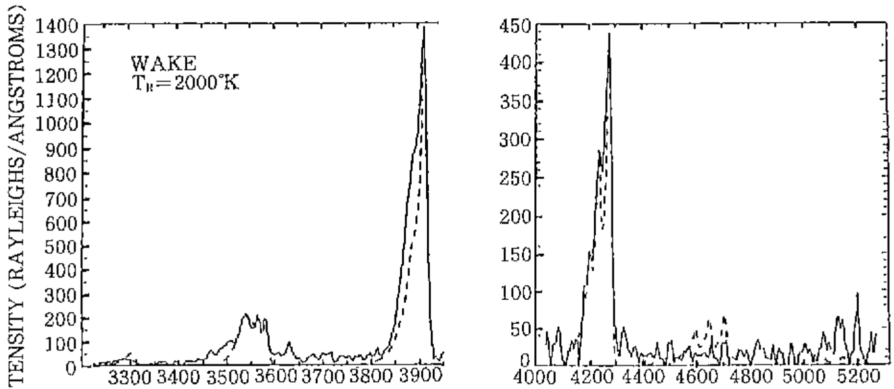

**Fig. 4.** Synthetic spectral fit to measured $N_2^+$ first negative bands obtained using a rotational temperature of 2000°K and the vibrational distribution shown in Fig. 5.

of Vallance Jones and Hunten(1960) and Broadfoot and Hunten(1966), that was discussed in Section I.

In order to determine the fit to the vibrational distribution exhibited by the data, each upper vibrational level(v′) has been scaled to achieve the closest fit to the observations(Figure 4). The vibrational distribution required for this fit is shown in Figure 5 and compared with diurnal

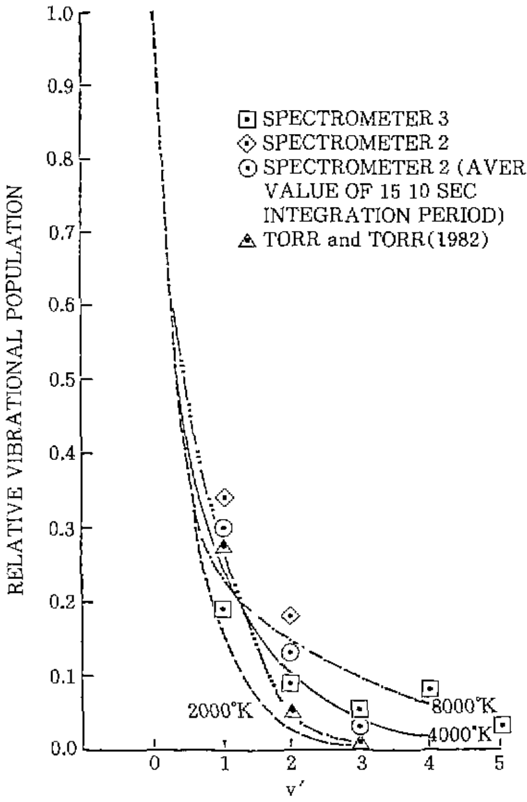

**Fig. 5.** Vibrational distribution obtained from data shown in Fig. 4 and thermal distributions for 2000°K, 4000°K and 8000°K are also shown.

vibrational distributions for 2000°K, 4000°K and 8000°K. Also shown in the figure for comparison is the theoretical distribution computed by Torr and Torr(1982). It can be seen from this figure that the data require very high apparent vibrational temperatures. In fact at $v'=1$ and 2, the $\triangle v=-1$ progression(measured somewhat earlier than $\triangle v=0$) would require Tv≥ =8000°K.

However, as can be seen from Figure 4, even with the best fit to the vibrational distribution, the width of the bands is still not well reproduced for $T_R=2000$°K. Figure 6a shows the synthetic spectral fit to the data using $T_R=4000$°K. Figure 6b shows the fit to the data using a rotational temperature of 900°K and Figure 7 shows $T_R=2800$°K. It appears from these data that a rotational temperature≥2800°K is required. The synthetic spectrum for $T_R=4000$°K begins to exceed the envelope of the data. When the asymmetry of the instrument response func-

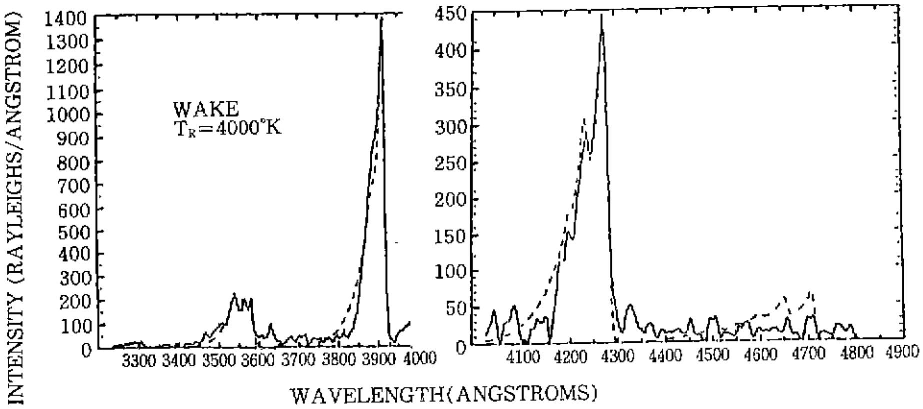

**Fig. 6a.** Same as Fig. 4 but with $T_R$=4000°K.

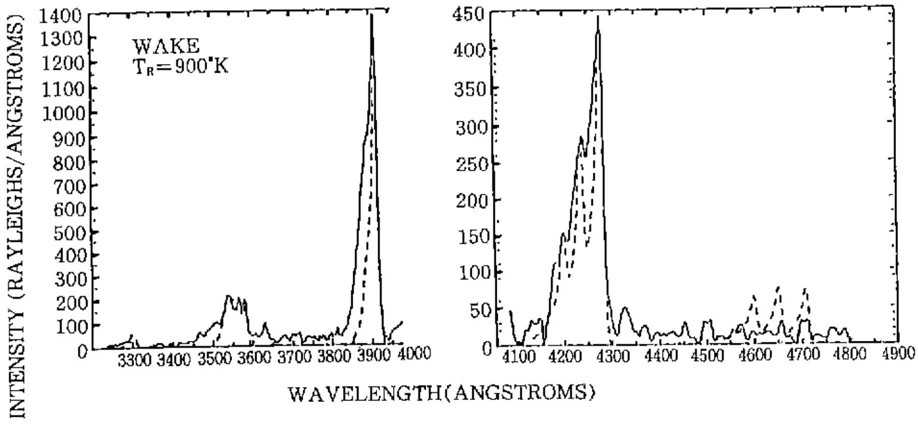

**Fig. 6b.** Same as Fig. 4 but with $T_R$=900°K.

tion for the NUV spectrometer is taken into account, the fit to the 0-0 band will be improved and a rotational temperature of approximately 2800°K should yield the best fit. The $\Delta v=0$ progression is valuable for setting the population of the 0 level. The $\Delta v=+1$ progression is perhaps the most useful of all, allowing a determination of $v'$ populations out to $v'=5$. It can be seen that even with the best fit to the vibrational and rotational populations, we do not get a good fit to short wavelength edge of the $\Delta v=0$ progression. We can say that this difference may be explained by an atomic helium line blended with this band system.

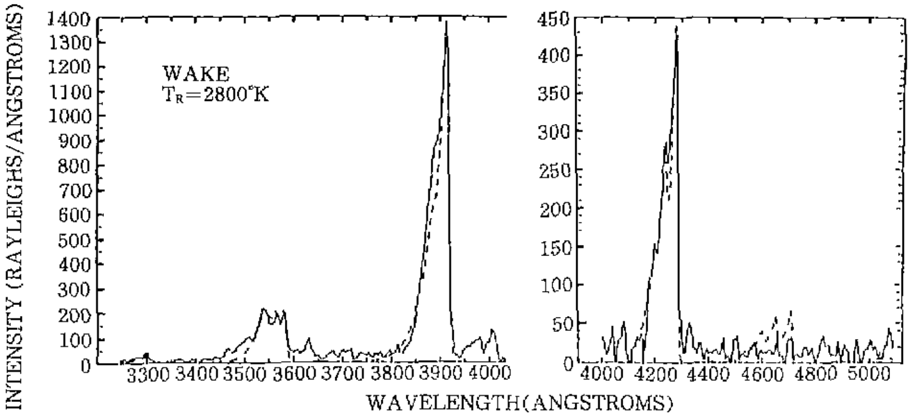

**Fig. 7.** Same as Fig. 4 but with $T_R=2800°K$.

## Ⅳ. Summary and Discussion

In this study we have investigated several of $N_2^+(1N)$ bright emissions of the high altitude thermospheric dayglow. The $N_2^+$ first negative system is found to be much brighter than anticipated and to be surprisingly enhanced in apparent vibrational temperature. The vibrational enhancement is present in wake viewing geometry. As a result we are unable to determine whether the unanticipated structure is a natural phenomenon, present in the ambient thermosphere, or whether we are seeing the results of a vehicle/ambient atmosphere interaction. However, we have not been able to identify any natural source of the $N_2^+$ emission that would be this persistent and yet have escaped detection in earlier observations of the first negative system(even though these were rather limited in this spectral coverage) or the $N_2^+$ ions. It would therefore appear reasonable to conclude at this point, that a likely source of the enhanced emission is the vehicle itself in its passage through the upper atmosphere and ionosphere. Since the $N_2^+$ first negative bands are not seen in the nighttime data, the mechanism must involve enhanced photoionization of an $N_2$ "cloud" or charge exchange with enhanced plasma densities on the dayside.

## Reference

Abdou, W. A., Torr, D. G., Richards, P. G., and Torr, M. R. 1982, The effect on thermospheric chemistry of a resonant charge exchange reaction involving vibrationally excited $N_2^+$ ions with atomic oxygen, *J. Geophys. Res.*, **87**, 6324.

Abdou, W. A., Torr, D. G., Richards, P. G., Torr, M. R., and Breig, E. L. 1984, Results of a comprehensive study of the photochemistry of $N_2^+$ in the ionosphere, *J. Geophys. Res.*, **89**, 9069.

Bates, D. R. 1949a, The intensity distribution in the nitrogen band systems emitted from the earth's upper atmosphere, *Proc. Roy. Soc.*(London), **A196**, 217.

________ 1949b, The emission of the negative system of nitrogen from the upper atmosphere and the significance of the twilight flash in the theory of the ionosphere, *Proc. Roy. Soc. (London)*, **A196**, 562.

Breig, E. L., Hanson, W. B., Hoffman, J. H., and Abdou, W. A. 1983, Photochemistry of $N_2^+$ in the daytime F region, *J. Geophys. Res.*, **38**, 7190.

Broadfoot, A. L., and Hunten, D. M. 1966, $N_2^+$ emission in the twilight, *Planet. Space Sci.*, **14**, 1303.

Fox, J. L., and Dalgarno, A. 1985, The vibrational distribution of $N_2^+$ in the terrestrial ionosphere, *J. Geophys. Res.*, **90**, 7557.

Herzberg, G. 1950, Molecular spectra and molecular structure, I. Spectra of Diatomic Molecules, 2nd ed.(Van Nostrand: New York).

Johnsen, R., and Biondi, M. A. 1980, Laboratory measurements of the $O^+(^2D)+N_2$ and $O^+(^2D)+O_2$ reaction rate coefficients and their ionospheric implications, *Geophys. Res. Lett.*, **7**, 401.

McFarland, M. 1974, Energy dependence and branching ratio of the $N_2^+ + O$ reaction, *J. Geophys. Res.*, **79**, 2925.

Oppenheimer, M., Dalgarno, A., and Brinton, H. C. 1976, Ion chemistry of $N_2^+$ and the solar ultraviolet flux in the thermosphere, *J. Geophys. Res.*, **81**, 3762.

Orsini, N. 1977, The vibrationally excited $N_2^+$ ion and the twilight 4278 A emission band in the earth's mid-latitude thermosphere, Ph. D. Thesis(University of Michigan: Ann Arbor).

Rowe, B. R., Fahey, D. W., Fehsenfeld, F. C., and Albritton, D. L. 1980, Rate constants for the reactions of metastable $O^{+*}$ ions with $N_2$ and $O_2$ at collision energies 0.04 to 0.2 eV and the mobilities of these ions at 300K, *J. Chem. Phys.*, **73**, 194.

Saha, M.N. 1937, On the action of ultraviolet sunlight upon the upper atmosphere, *Proc. Roy. Sci.(London)*, **A160**, 155.

Slipher, V.M. 1933, Spectrographic studies of the planets, *Mon. No. Roy. Astron. Soc.*, **93**, 657.

Stormer, P. 1939, Blue auroral rays situated in the sunlit part of the atmosphere, *Terr. Magn.*, **44**, 7.

Swings, P. 1949, The spectra of the night sky and the aurora, The Atmospheres of the Earth and Planets, ed., G.P. Kuiper, Chapter Ⅵ, 159.

Torr, D.G. 1979, Ionospheric Chemistry, *Rev. Geophys. Space Phys.*, **17**, 510.

Torr, D.G., and Torr, M.R. 1980, Determination of the thermal rate coefficients products and branching ratios for the reaction of $O^+(^2D)$ with $N_2$, *J. Geophys. Res.*, **85**, 783.

Torr, M.R., and Torr, D.G. 1982, The role of metastable species in the thermosphere, *Rev. Geophys. Space Phys.*, **20**, 91.

Torr, M.R., and Torr, D.G. 1985, Ionization frequencies for solar cycle 21: revised, *J. Geophys. Res.*, **90**, 6676.

Vallance Jones, A., and Hunten, D. M. 1960, Rotational and vibrational intensity distribution of the first negative $N_2^+$ bands in sunlit auroral rays, *Can. J. Phys.*, **38**, 458.

Walker, J.C.G. 1973, Physics and Chemistry of Upper Atmosphere, B.M. McCormac. ed.(D. Reidel Publishing Company: Dordrect), 203.

Wulf, O.R., and Deming, L.S. 1983, In the production of the ionospheric regions E and F and the lower-altitude ionization causing radio fadeouts, *J. Geophys. Res.*, **43**, 283.