Theoretical Estimation of the Vibrational Temperatures of N_2 Molecules in the Ionosphere and in the Laboratory Simulated plasma

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The vibrational temperature of excited nitrogen molecules (N_2*) are estimated theoretically for the case of ionosphere as well as for the laboratory simulated plasma, considering the various chemical reactions leading to the production and loss of N_2 molecules. It has been found that even in the case when quenching of the excited molecules by O and CO_2 is considered, the vibrational temperature T_v is higher than the neutral temperature T_n below about 105 km but the difference decreases and about 120 km, the value of T_v is less than T_n. However, for no quenching case, the vibrational temperature can be as high as 1600°K at 150 km. The vibrational temperature for the laboratory simulated plasma on the other hand was found to be considerably high (1500°K or more), the absolute value being dependent upon the concentration of O_2 in the gas mixture taken and the intensity of UV light used for excitation of nitrogen molecules.

1. INTRODUCTION

The vibrational temperature of N_2 molecules play an important role in the energy budget of the thermosphere. A number of processes in this region can be significantly influenced by the enhanced vibrational contents of N_2. It is also believed that enhanced vibrational excitation of N_2 can significantly affect the cooling rates of thermal electrons [1]. Vibrationally excited N_2 is also suggested to be the main heating mechanism in the E-region of the ionosphere [2] to explain experimentally observed higher electron temperatures [3]. To explain the influence of N_2 vibration, an estimate of vibrational temperature is required. Many workers [4, 5, 6, 7] have suggested large vibrational temperatures of N_2 (T_v) which in turn if considered, can significantly affect the electron cooling rates. However, their work did not include the quenching of vibrationally excited N_2 by atomic oxygen which is now considered an important loss mechanism for the same [8] and can result in the T_v to be not much different from neutral temperature.

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The simulation of ionospheric plasma in the laboratory also demonstrated the existence of a strong coupling between vibrationally excited nitrogen molecules and the energy distribution function of electrons [9, 10, 11, 12]. The vibrational temperature T_v in this case which depends upon the degree of vibrational excitation as determined by electric field to the gas density ratio (E/N) and the degree of ionization (e/N) are still found to be higher than those inferred for appropriate atmospheric conditions [13].

In the present work therefore, an attempt has been made to estimate theoretically the vibrational temperatures of N_2^*, first, in the atmospheric E-region demonstrating the effect of quenching of N_2^* by atomic oxygen and CO_2; considering the various chemical reactions contributing to the production and loss of N_2^* molecules. Next, the same approach is used to estimate the T_v for the laboratory simulated plasma. The inferred values are compared with the experimentally measured values [13] and the various uncertainties in the experimental and theoretical determination of T_v are discussed.

2. METHOD

The various chemical reactions which can contribute to the production and loss of N_2^* molecules and their laboratory measured reaction rates are shown in Table I. Since the main source of excitation of N_2 molecules in the atmosphere is O^1D which in turn is produced mainly by photo-dissociation of molecular oxygen in the Schumann-Runge continuum of the UV radiation, the various reactions leading to the production and loss of this species are also considered.

The concentrations of O^1D and N_2^* molecules are estimated by considering their continuity equations taking into account the contributions from various chemical reactions to their production and loss terms as

$$dn[O^1D]/dt = (J1+J2)[O_2]+J3[O_3]+J14[NO_2]+K1[O_2^+][e]-[O^1D]$$

$$\{K2[O_3]+K3[N_2]+K4[O_2]+K5[H_2O]+K6[H_2]\} \tag{1}$$

$$dn[N_2^*]/dt=K3[N_2][O^1D]+K8[N][NO]-[N_2^*]\{K9[e]+K10[CO_2]$$

$$+K11[M]+K7[O]+K12[O_2]\} \tag{2}$$

where various J and K are the photo-dissociation and reaction rates respectively and terms in the brackets represent concentration of those species. The loss of these species due to transport, arising essentially due to diffusion is neglected in the present study as its contribution is expected to be insignificant below about 200 km [1]. Further, it is assumed that both the species O^1D and N_2^* are

in equilibrium i.e. $dn[O^1D]/dt$ and $dn(N_2^*)/dt$ terms are equal to zero. The concentration of each of these species can then be estimated from equation (1) and (2).

In the laboratory simulation of ionospheric plasma, however, there are various other mechanisms contributing to the loss and production of N_2^*, in addition to the chemical reactions given in Table I. Some of the additional reactions need to be considered are due to some impurities such as of CO_2, CH_4 or oxides of nitrogen present in the gas mixtures used. These reactions and their laboratory measured reaction rates which were also considered in this study are listed in Table II. Since in this case atomic oxygen and ozone are not naturally present but are produced as a result of photo-dissociation of molecular oxygen by uv source and subsequent reactions, their concentrations were also estimated in this case so as to account properly, quenching of N2*.

At low pressure, besides the different chemical reactions between various chemical species in the chamber, the quenching of active centers or radicals such as O and O^1D by chamber walls should also be considered. This quenching acts as an important loss mechanism by converting these active centers into inactive molecules [29, 30, 31]. The destruction time of these active centers due to wall effect is primarily controlled by their diffusion time and is given by [32]:

$$T = 4\ D^2/(\pi^2\ \lambda\ v) \tag{3}$$

where D is the chamber diameter, λ is the mean free path and v is the molecular speed. In the present work, the destruction time as given by equation (3) is used.

Yet another effect of the chamber walls is possible due to which the excited nitrogen molecules can loose their partial energies due to collision with the chamber walls. The possible mechanism for this process is given by [33]:

$$N_2(v) + wall \rightarrow N_2\ (v-1) + wall + K.E. \tag{4}$$

Since in the present work, the population of excited molecules are considered as a whole and not individually, it is assumed that this effect may affect the relative population in different excitation levels but does not alter the total concentration or population of excited nitrogen molecules.

The vibration temperature of nitrogen molecules in the excited states is then determined from the following expressions [4]:

$$T_v = \theta\ /\ [\ \ln\{(1 + \epsilon)/\epsilon\ \}] \tag{5}$$
and
$$\epsilon = [N_2^*]/[N_2] \tag{6}$$

where θ is the characteristic vibrational temperature of nitrogen molecules

Table I

No.	Reaction	Rate*	Reference
J1	$O_2 + h\nu \rightarrow O + O^1D$ (135–175 nm)	2.0×10^{-6}	[14]
J3	$O_2 + h\nu \rightarrow O + O$ (205-242 nm)	1.04×10^{-9}	[21]
J5	$O_3 + h\nu \rightarrow O_2{}^1{}_{\Delta g} + O^1D$ (97–310 nm)	9.63×10^{-13}	[15]
J14	$NO_2 + h\nu \rightarrow NO + O^1D$ (102.7–244 nm)	1.22×10^{-4}	[20]
K1	$O_2{}^+ + e \rightarrow O + O^1D$	$2.21 \times 10^{-7}(T_e/300)^{-0.76}$	[16]
K2	$O_3 + O^1D \rightarrow O_2 + O_2$	2.70×10^{-10}	[17]
K3	$N_2 + O^1D \rightarrow N_2{}^* + O$	2.30×10^{-11}	[18]
K4	$O_2 + O^1D \rightarrow O + O_2$	7.4×10^{-11}	[17]
K5	$H_2O + O^1D \rightarrow OH + OH$	3.50×10^{-10}	[17]
K6	$H_2 + O^1D \rightarrow H + OH$	2.90×10^{-10}	[17]
K7	$N_2{}^* + O \rightarrow N_2 + O + h\nu$	3.20×10^{-15} at 300°K	[8]
K8	$N + NO \rightarrow N_2{}^* + O$	4.0×10^{-11}	[26]
K9	$N_2{}^* + e \rightarrow N_2 + e + h\nu$	5.0×10^{-11}	[27]
K10	$N_2{}^* + CO_2 \rightarrow N_2 + CO_2{}^*$	4.50×10^{-13}	[28]
K11	$N_2{}^* + M \rightarrow N_2 + M + h\nu$	$1.3 \times 10^{-11}T_n\exp(-220/T_n{}^{0.33})$	[5]
K12	$N_2{}^* + O_2 \rightarrow O_2{}^* + N_2$	$2.5 \times 10^{-7}\exp(-263/T_n{}^{0.33})$ $/(1-\exp(3390/T_n)$	[5]

These J values correspond to unattenuated values at the top of the atmosphere.

Table II

No.	Reaction	Rate*	Reference
J2	$O_2 + h\nu \rightarrow O + O$ (175–205 nm)	1.87×10^{-7}	[*19*]
J6	$O_3 + h\nu \rightarrow O + O_2{}^1{}_{\Delta g}$ (310-360 nm)	1.25×10^{-4}	[*22*]
J7	$O_3 + h\nu \rightarrow O + O_2$ (405–850 nm)	3.4×10^{-4}	[*14*]
J13	$NO_2 + h\nu \rightarrow NO + O$ (244–398 nm)	6.90×10^{-3}	[*14*]
J20	$CH_4 + h\nu \rightarrow CH_3 + H$ (80–160 nm)	1.06×10^{-5}	[*14*]
K13	$O_3 + O^1D \rightarrow O + O + O_2$	2.70×10^{-10}	[*17*]
K14	$N + NO_2 \rightarrow O + O + N_2$	2.40×10^{-12}	[*23*]
K15	$O + O + M \rightarrow O_2 + M$	$4.8 \times 10^{-33}(T_n/300)^{-2.0}$	[*14*]
K16	$O + O_2 + M \rightarrow O_3 + M$	$6.20 \times 10^{-34}(T_n/300)^{-2.0}$	[*14*]
K17	$O + O_3 \rightarrow O_2 + O_2$	$1.5 \times 10^{-11}\exp(-2718/T_n)$	[*14*]
K18	$NO_2 + O \rightarrow NO + O_2$	9.3×10^{-12}	[*14*]
K19	$O + NO_2 + M \rightarrow NO_3 + M$	$9.0 \times 10^{-32}(T_n/300)^{-2.0}$	[*14*]
K20	$H_2 + O \rightarrow H + OH$	$3.0 \times 10^{-14}\exp(-4480/T_n)$	[*24*]
K21	$CH_3 + O \rightarrow CH_2O + H$	1.3×10^{-10}	[*14*]
KW	$O + O + wall \rightarrow O_2 + wall$	KW	See text
KW	$O^1D + O^1D + wall \rightarrow O_2 + wall + K.E.$	KW	See text
K22	$O_3 + CH_3 \rightarrow Product$	2.6×10^{-12}	[*25*]
K23	$CH_3 + O_2 + M \rightarrow Prod + M$	$2.2 \times 10^{-31}(T_n/300)^{-2.2}$	[*14*]

*where the units are s^{-1}, $cm^3\ s^{-1}$ and $cm^6\ s^{-1}$ for one body, two body and three body reactions respectively.

and is equal to 3400°K. These calculations are based on the assumption that contribution due to diffusion is negligibly small compared with chemical loss rates which is quite true for lower altitude region in the atmosphere [4]. Since the laboratory simulation of the plasma too correspond to atmospheric conditions of lower E-region (pressure is 10^{-2} torr which correspond to about 88 km of altitude) the same assumption should hold good for this case as well.

In the case of laboratory plasma simulation, the plasma is first created by the ionizing source with different compositions of N_2 and O_2 gases. Since the ionizing source makes use of an electric field, the same can also influence to some extent the excitation of nitrogen molecules. The degree of excitation of N_2 molecules depends upon the ratio of electric field to concentration of N_2 molecules and degree of ionization [34]. Thus the nitrogen molecules in the case of laboratory plasma will have some residual vibrational temperature arising essentially due to the effect of electric field for creating the plasma itself. Experimentally, this residual temperature is found to be about 1500°K [36]. Next, when the uv light source is switched on, the N_2 molecules are further excited and the concentrations of $N_2{}^*$ molecules and T_v increase further. To account for this residual T_v in the present study, first the $N_2{}^*$ concentration corresponding to residual T_v is determined from equations (5) and (6) and then this residual concentration of $N_2{}^*$ is added to the value computed based on purely chemical considerations as given by equation (2). Finally, from the total effective $N_2{}^*$, the effective T_v and hence the increase in T_v due to uv light source is estimated as:

$$T_v = T_{v\ on} - T_{v\ res.} \tag{7}$$

where $T_{v\ on}$ is the vibrational temperature when the uv source is put on and $T_{v\ res.}$ is the residual vibrational temperature essentially due to the effect of electric field arising due to the use of ionizing source.

3. RESULTS AND DISCUSSION

The vibrational temperature of $N_2{}^*$ molecules was estimated for the atmospheric E-region in the altitude range 90 to 150 km. These calculations were carried out for latitude of 31.25° corresponding to Uchinoura and for conditions appropriate to Feb. 13, 1982, 11 o'clock JST for which some experimental data regarding electron density etc. are available from the rocket flight [13]. MSIS-86 model [35] appropriate to flight conditions was adopted for the concentrations of neutral constituents whereas for nitric oxide, values suggested by Ogawa et al [36] were used. The carbon dioxide values were taken from the work of Hays & Olivero [37]. The vibration temperature profiles thus derived are shown in Fig. 1. For comparison, the results obtained by other workers [2, 4, 5, 7] are also shown in the same figure. To see the effect of various quenching mechanisms including O and CO_2 on T_v, different cases were considered including (i) Quenching both, by O and CO_2 (ii) quenching by O only (iii)
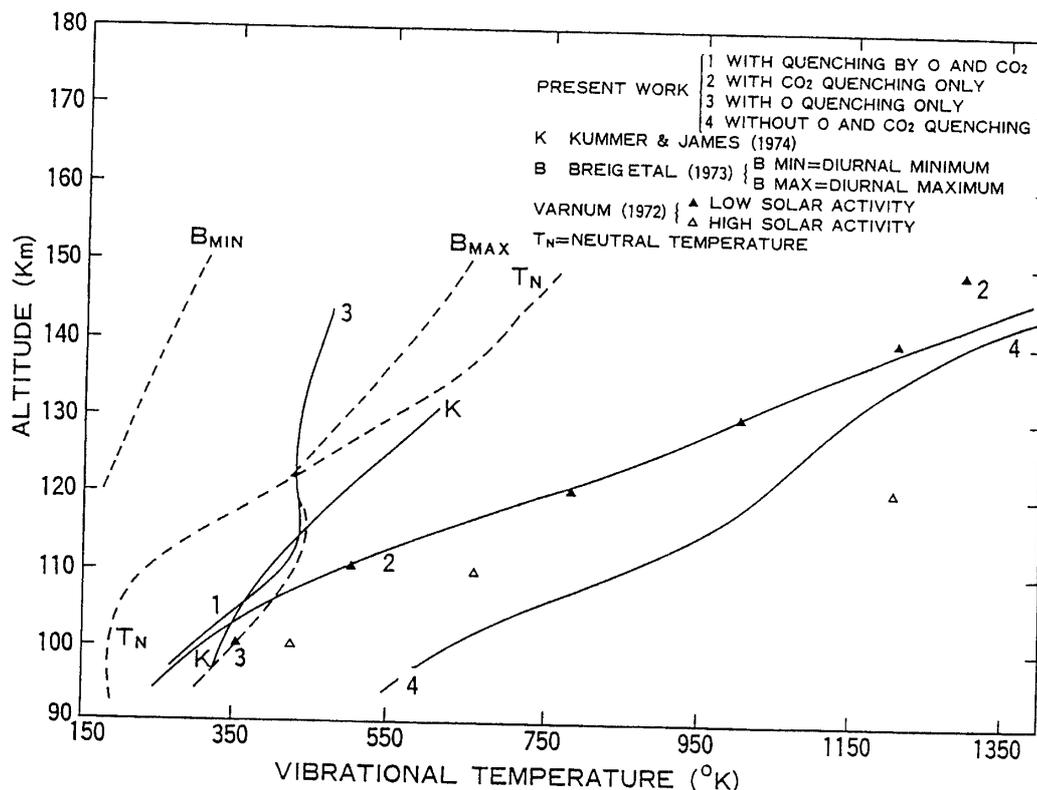
Fig. 1. Variation of vibrational temperature with altitude in the atmosphere. Four cases were considered namely, (i) with quenching both by O and CO_2 shown as curve 1 (ii) with quenching by CO_2 only (curve 2) (iii) with quenching by O only depicted as curve 3 and (iv) with no quenching shown as curve 4. The results obtained by other workers are also shown in the same figure for comparison.

quenching by CO_2 only and (iv) no quenching at all. These considerations allow us to compare our results with those obtained by other workers, who have considered one or the other quenching mechanism but not all resulting some time in much higher value of T_v.

It may be seen that in case of quenching by O and CO_2 shown as curve 1, T_v is little higher than neutral temperature T_n up to about 105 km but above this altitude, the difference decreases and at 120 km T_v becomes equal to T_n. In the higher altitude range, T_v however does not change much but remains less than T_n. The relative decrease in T_v compared to T_n is mainly due to quenching by O which has its quenching rate dependent upon T_n [8]. These values when compared with those of Kummer and James [28] show fairly good agreement up to about 115 km but above, the later values are high. The difference, it is felt is partly due to the neutral density model used particularly for O which is found to be low by a factor of 5 compared to MSIS model adopted in the present case. Breig et al [38] have suggested a range of T_v for diurnal maximum and diurnal minimum taking in to account the effect of quenching by O in their calculations. Our derived values, as may be seen lie well within this suggested range. It may however be pointed out that these people had not con-
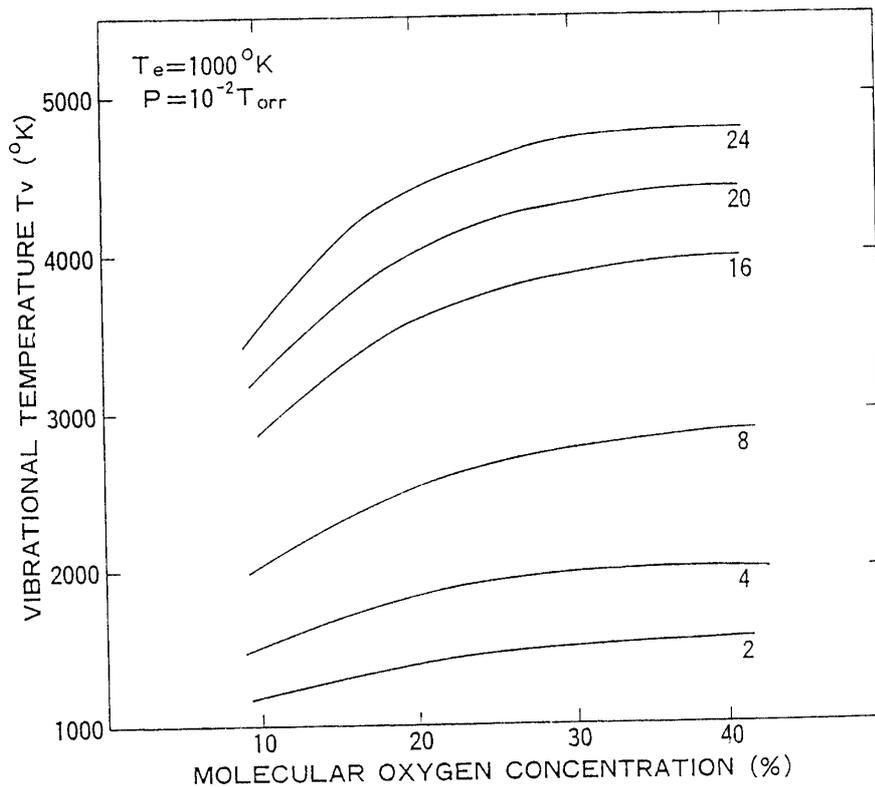
Fig. 2. Vibrational temperature dependence on O_2 concentration in the N_2-O_2 gas mixture for the laboratory simulated plasma for different numbers of uv lamps switched on simultaneously.

sidered reaction (K3) which according to present estimate contribute about 30~40% to the production of N_2^* above 120 km. Also the use of Jacchia model [*39*] for the neutral species instead of MSIS model is expected to introduce significant difference in T_v.

In case of quenching by O alone, the T_v values are found to be higher than the previous case by about 50°K at 100 km (curve 3). This difference decreases with increase of altitude and above 120 km, there is no difference at all between the two curves i.e. 1 & 3. It is so because in the lower altitude region, by considering the quenching by O only and not by CO_2, the significant loss of N_2^* does not take place resulting in higher T_v.

Similarly, when O quenching is not considered but CO_2 quenching is included represented by curve 2 in Fig. 1, the derived values of T_v show a sharp increase above about 105 km and become as high as 1395°K at 145 km. The production of N_2^* above 120 km is due to reaction (K3) with equally important contribution coming from reaction (K8) while the loss by CO_2 quenching only is now very small due to lower CO_2 concentration. This results in higher N_2^* concentration and hence higher T_v.

Varnum [*6*] had considered quenching of N_2^* by CO_2 only in his calculations of T_v for low and high solar activity. A comparison of his values for low solar activity with those derived in the present study shows an excellent agreement throughout the altitude range though our values are for high solar activity ($F_{10,7}$ = 193 units). The high solar activity values of Tv [*6*] are considerably
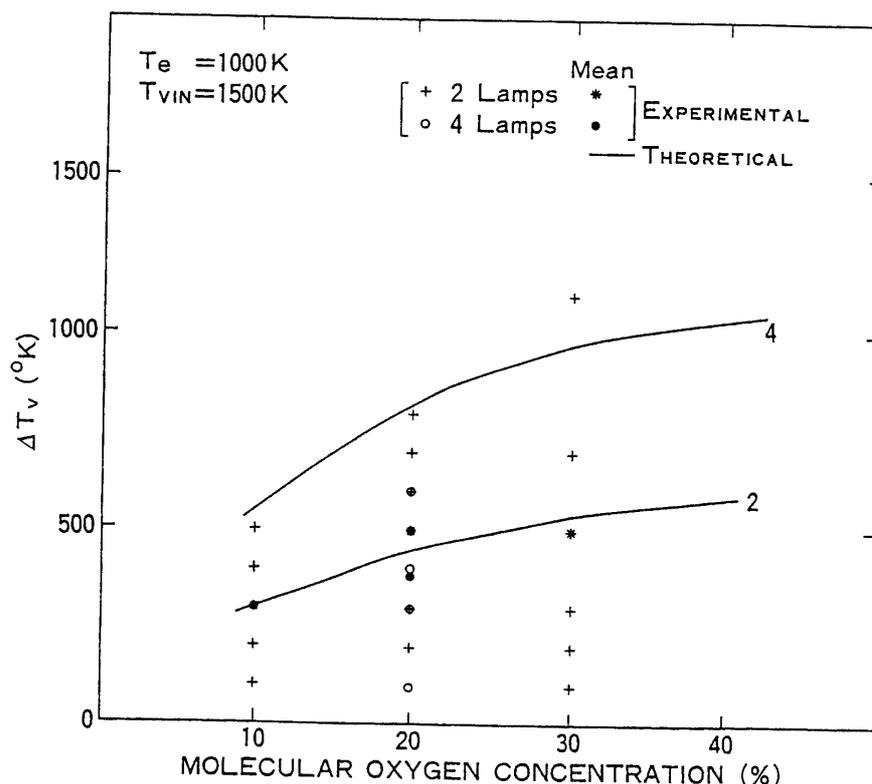
Fig. 3. Effective increase in vibrational temperature of plasma as a function of O_2 concentration for two and four lamps. Residual vibrational temperature of 1500°K caused by the application of electric field due to ionization source was considered.

high, the difference being by about 120°K at 100 km and increasing to about 650°K at 150 km. This large change is felt to be due to the over-estimation of O^1D in his model and the quenching of the same leading to the production of N_2^*. For high solar activity, his calculations show much higher production of N_2 vibration quanta by O^1D than in the present case, probably due to high concentration of O^1D. Also the quenching rate of O^1D by N_2 used by him is almost twice the value adopted in this work.

Same is the case when even CO_2 quenching is also not considered. Under this condition the loss mechanisms operating on N_2^* are due to electrons, N_2 and O_2 which are even much less significant thereby cause the T_v to increase further. In the lower region too, the increase in T_v values is even higher because of no loss of N_2^* by CO_2.

Next, the calculations for the case of laboratory plasma were performed for different number of uv lamps put on simultaneously to excite N_2 molecules and for different percentage of O_2 in the N_2–O_2 gas mixture. Fig. 2 shows the variation of T_v as a function of % O_2 concentration for different number of lamps used. It is found that vibrational temperature increases with the increase of O_2 concentration more steeply up to about 20% and then less rapidly beyond. The degree of steepness increases as more number of lamps are used to excite the N_2 molecules. It is due to the fact that up to 20%, more and more of O^1D is produced whereas the concentration of O is still not adequate for the quenching

to be important and this result in higher concentration of N_2^* and hence T_v. As the concentration of O_2 is further increased, the O concentration becomes appreciable and starts quenching N_2^*. More number of lamps used add to the light intensity and cause more and more excitation of N_2 molecules. However a limit is reached when light intensity is enough to excite almost all the nitrogen molecules and the O generated due to photo-dissociation of O_2 by the same light, quenches them. At this stage, the T_v is almost constant.

To simulate the vibrational temperature of N_2 for the laboratory plasma when separate ionization source was used, a residual vibrational temperature of 1500°K as determined experimentally [13] was used and increase in the vibrational temperature ΔT_v for known number of uv lamps was estimated. The derived ΔT_v along with experimentally observed values [13] as a function of O_2 concentration are shown in Fig. 3. Two cases of two and four lamps were considered for which some experimental data is available. The experimental data seems to show large scatter in ΔT_v probably as a result of oscillations in the plasma generated when the photons from the light source impinge upon the gas molecules and excite them. In view of this scatter in the observed data, the mean values are considered for comparison.

The change in vibration temperature ΔT_v, as may be seen also exhibit the same pattern of variation with O_2 concentration as in the previous figure i.e. increasing steeply up to about 20% concentration and then rather slowly tending to a constant value. The mean value from observed data for two lamp case lie quite close to the estimated values. However for four lamp case, the mean experimental values are significantly low essentially due to availability of very few observations and that too with large scatter. It may be mentioned that absolute value of ΔT_v in the present estimate depend mainly on the residual T_v which in itself could have large uncertainties.

4. CONCLUSIONS

The theoretical estimate of T_v show good agreement with the values reported by other workers provided due considerations are given for the difference in the models used and reactions considered. The vibration temperature in the lower altitude range below about 120 km is certainly higher than the neutral temperature even if quenching by O and CO_2 are considered. This enhanced value of T_v can act as an important heat source for the thermal electrons in the lower E-region and may explain to some extent the experimentally observed high electron temperatures.

The laboratory simulation of plasma clearly shows that for low O_2 concentration, the quenching by O is not so important loss mechanism and T_v increases with O_2 concentration. However, as the light intensity and O_2 concentration are increased, the O production increases and quenching by O comes in to play and causes T_v to vary less rapidly or it remains more or less constant.

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