THEORETICAL N₂ VIBRATIONAL DISTRIBUTION IN AN AURORA

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Abstract—The N_2 vibrational distribution in an aurora is investigated. During the auroral bombardment the vibrational distribution is non-Boltzmann. The deviation from the Boltzmann distribution increases with increasing altitude. Above 200 km the loss rate of O^+ due to the reaction $O^+ + N_2 \rightarrow NO^+ + N$ is increased by a factor of 1·5 when allowance is made for the non-Boltzmann character of the N_2 distribution. This increased loss rate persists for 1000–2000 sec after auroral bombardment commences.

1. INTRODUCTION

During auroral bombardment electrons in the energy range 3 to 6 eV have sufficient energy to excite the vibrational levels of N_2. The production into a given level depends on the magnitude of the nonthermal electron flux and the vibrational cross sections. Vibrational exchange in N_2–N_2 collisions tends to redistribute the vibrational quanta until a Boltzmann distribution is attained. However, for the large nonthermal electron fluxes that may occur during auroral bombardment, the production in a given vibrational level may be large. Consequently, non-Boltzmann N_2 vibrational distributions may persist in an auroral atmosphere for some time. It is the purpose of this paper to calculate the N_2 vibrational distribution for an auroral model and to follow the relaxation to a Boltzmann distribution.

2. THEORETICAL FORMULATION

Walker (1968) and Walker *et al.* (1969) have shown that, in the *E*- and *F*-regions of the ionosphere, electron quenching of nitrogen vibration is considerably more rapid than either quenching in collisions with N_2, O_2, O, He, and H or exchange of vibrational quanta in collisions with O_2, NO and H_2. An expression for the lifetime, τ_e, of nitrogen molecules in the first vibrational level against quenching by ionospheric electrons is given by

$$\tau_e = 2 \times 10^9 T_e^{1/2} \left[1 + \frac{T_e}{6500} \right]^2 \left[n_e \left(1 + \frac{T_e}{2200} \right) \right]^{-1}$$

where n_e is the electron density and T_e is the electron temperature (Walker, private communication). Using this expression we obtain for our auroral model $\tau_e > 5 \times 10^4$ sec at all altitude levels. The lifetimes of the higher vibrational levels are longer (Chen, 1964). Consequently, for time periods less than 5×10^4 sec quenching by ambient thermal electrons will have a negligible effect on the vibrational distribution of molecular nitrogen.

There are two other processes which may affect the vibrational distribution of molecular nitrogen in the ionosphere. These are carbon dioxide quenching at low altitudes and molecular diffusion at high altitudes (cf. Walker *et al.*, 1969). For altitudes of interest in this paper (greater than 150 km), carbon dioxide quenching is negligible. The effect of vertical diffusion is neglected and an estimate of the resultant error is presented later.

With the above simplifications the equation describing the density of molecules, n_r, in

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vibrational state r is given by

$$\frac{dn_r}{dt} = \sum_{s=1}^{11} \{k_{r+1,r}^{s-1,s}n_{r+1}n_{s-1} - k_{r,r+1}^{s,s-1}n_r n_s\} - \sum_{s=0}^{10} \{k_{r,r-1}^{s,s+1}n_r n_s - k_{r-1,r}^{s+1,s}n_{r-1}n_{s+1}\} + Q_r \quad (1)$$

where $k_{a,b}^{c,d}$ is the rate coefficient for the process

$$n_a + n_c \rightarrow n_b + n_d \quad (2)$$

in which vibrational energy is exchanged, and Q_r is the rate of production of molecules in vibrational state r due to photoelectron impact. In deriving (1) we assumed that only single quantum jumps are important. This should be a good assumption for neutral gas temperatures of ionospheric interest (cf. Treanor, Rich and Rehm, 1968; Fisher and Kummler, 1968).

The calculation of the rate coefficients, $k_{a,b}^{c,d}$, requires a model for the vibrational energy spacing in the N_2 molecule. For our calculations we will assume harmonic vibrational quantum states. The difference between the harmonic and anharmonic models of N_2 has been discussed by Treanor, Rich and Rehm (1968) and Fisher and Kummler (1968). In the steady state the difference in the vibrational populations of the first eleven states is small for translational ($T \sim 1000°K$) and vibrational ($1800 \leq T_v \leq 3800°K$) temperatures of interest in this paper.

The vibration–vibration exchange probabilities can be calculated using the colinear model of Rapp and Englander-Golden (1964). In the harmonic model there is no energy defect and the energy-transfer probability per collision is given by (cf. Fisher and Kummler 1968)

$$P_{a,b}^{c,d} = \frac{16\pi^2 \mu^2 L^2 v_{ab}^2 v_{cd}^2}{h^2} v^2 \quad (3)$$

where v is the initial relative velocity of the colliding molecules, μ is the reduced mass, h is Planck's constant, $L = 2 \times 10^{-9}$ cm and the v_{ab} are the harmonic-oscillator matrix elements (Sharp and Rapp, 1965). The rate coefficient is obtained by integrating the probability per collision over the collision frequency and a one-dimensional, Maxwellian distribution of relative velocities (Rapp, 1960),

$$k_{a,b}^{c,d} = 24\sqrt{2\mu} \frac{\pi^{7/2} L^2 \sigma^2}{h^2} v_{ab}^2 v_{cd}^2 (kT)^{3/2} \quad (4)$$

where k is Boltzmann's constant and σ is the hard sphere collision diameter ($\sigma^2 = 14 \times 10^{-16}$ cm² for N_2).

The harmonic-oscillator matrix elements satisfy the relations

$$v_{ab} = v_{ba} \quad (5)$$

and

$$v_{j+1,j}^2 = (j+1)v_{1,0}^2 \quad (6)$$

(Sharp and Rapp, 1965). Consequently, all the rate coefficients can be expressed in terms of $k_{1,0}^{0,1}$. With this simplification Equation (1) becomes

$$\frac{dn_r}{dt} = k_{1,0}^{0,1} \left\{ [(r+1)n_{r+1} - rn_r] \sum_{s=1}^{11} sn_{s-1} + [rn_{r-1} - (r+1)n_r] \sum_{s=1}^{11} sn_s \right\} + Q_r. \quad (7)$$

In the analysis that follows we consider a 12 level system consisting of the ground state and the first eleven vibrational states. The resulting system of coupled, nonlinear differential equations is solved using a numerical technique described by Bailey (1969).

3. APPLICATION TO THE IONOSPHERE

Walker *et al.* (1969) have calculated the sources of vibrational quanta for the aurora which occurred above Fort Yukon, Alaska, at 2100 AST on 26 February, 1961 (Belon, Romick and Rees, 1966). For this aurora, with an intensity of 30·6 kR of 3914 Å radiation, they found that the principle source is that provided by collisions with auroral secondary electrons.

Considering nonthermal electrons as the only source, we have calculated the production of vibrational quanta in the individual states using the equilibrium photoelectron fluxes presented by Dalgarno, McElroy and Stewart (1969) and the vibrational excitation cross sections given by Schulz (1964), Chen (1964), and Engelhardt, Phelps and Risk (1964). Since the vibrational cross sections are rapidly varying functions of energy, the production of vibrational quanta is not sensitive to the exact shape of the equilibrium flux. We have normalized our total production of quanta, at each altitude, to the values used by Walker *et al.* (1969) (Stolarski, private communication). We have found that quenching by the nonthermal flux has a negligibly small effect on the vibrational distribution.

The neutral atmosphere used was the model atmosphere of Jacchia (1964) as modified by Walker (1965) with an exospheric temperature of 1000°K. The initial vibrational distribution was assumed to be a Boltzmann distribution with $T_v = 1800°K$. The aurora is simulated by turning on the nonthermal electron flux at $t = 0$ and off at $t = 15$ min.

In Table 1 we show the time evolution, at 250 km, of the ratio of the population in level r to the population in the energetically equivalent Boltzmann distribution. Also shown in

TABLE 1. RATIO OF THE POPULATION IN LEVEL r TO THAT IN AN ENERGETICALLY EQUIVALENT BOLTZMANN DISTRIBUTION. ALTITUDE EQUALS 250 km

Level t(sec) = T_v(°K) =	10 1824	30 1878	50 1925	100 2049	150 2169	200 2287	300 2516	500 2959	925 3858	1975 3858
0	1·00	1·01	1·01	1·02	1·03	1·04	1·04	1·05	1·03	1·00
1	0·98	0·96	0·93	0·89	0·86	0·85	0·84	0·87	0·97	1·00
2	0·97	0·93	0·89	0·83	0·79	0·77	0·76	0·79	0·90	1·00
3	1·01	1·04	1·05	1·05	1·04	1·02	0·98	0·93	0·92	1·00
4	1·29	1·76	2·02	2·32	2·33	2 23	1·93	1·44	1·04	1·00
5	2·88	5·71	7·09	8·09	7·49	6·50	4·68	2·59	1·28	1·01
6	11·6	25·4	30·4	30·1	24·2	18·7	11·0	4·66	1·63	1·01
7	39·5	84·1	95·8	82·7	59·3	41·3	20·9	7·16	1·94	1·02
8	122·0	232·0	242·0	174·0	110·0	70·0	31·1	9·15	2·09	1·03
9	9·65	50·3	77·1	89·0	69·2	49·0	24·3	7·76	1·86	1·04
10	1·27	8·73	19·6	38·2	37·9	30·9	17·8	6·39	1·65	1·05
11	0·79	1·61	4·5	15·0	19·7	19·0	13·0	5·35	1·50	1·05

this table is the vibrational temperature of the Boltzmann distribution. The lower levels are underpopulated and the higher levels overpopulated relative to the Boltzmann distribution. The peak in the ratio at $r = 8$ occurs because we have not allowed for production of quanta in states 9, 10 and 11. Vibrational cross sections were not available for these states. The results above 250 km are similar with the magnitude of the effect greater and the duration longer. The reverse is true for the results below 250 km. Our calculations above 250 km, however, overestimate the population ratios of the higher levels because we have neglected the effects of diffusion (Walker *et al.*, 1969). Above this altitude level diffusion acts to reduce the population ratios because the N₂ molecules can diffuse to lower altitudes where the vibrational exchange rates are greater.

Schmeltekopf *et al.* (1966) have shown that the rate coefficient, k_r, for the reaction $O^+ + N_2 \rightarrow NO^+ + N$ is sensitive to the N_2 vibrational distribution. In Fig. 1 we compare
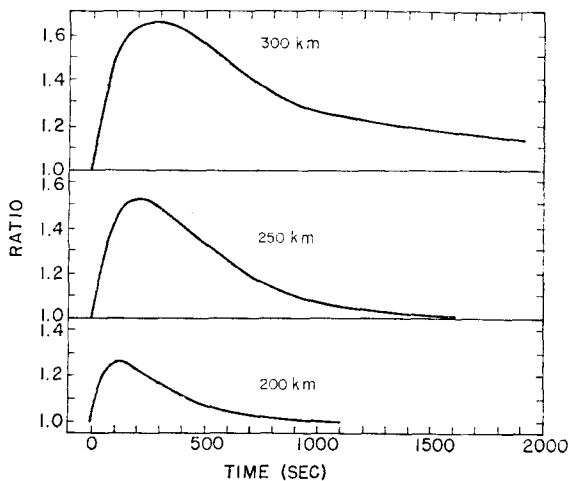

FIG. 1. THE RATIO OF THE NON-BOLTZMANN AND BOLTZMANN LOSS RATES FOR O^+.

the rate of loss of O^+, $\sum_r k_r n_r$, obtained by using the Boltzmann and non-Boltzmann distributions. At 250 km the non-Boltzmann loss rate is a factor of 1·5 greater than the Boltzmann loss rate. Using the Franck–Condon factors presented by Benesch *et al.* (1966), we have also compared the rate of population of the $C^3\pi_u$ state of N_2 by secondary electron impact using the Boltzmann and non-Boltzmann distributions. At all altitude levels the difference between the results is negligible.

In order to check the sensitivity of the results to the vibrational rate coefficient $k_{1,0}^{0,1}$, we have reduced the rate coefficient by a factor of two and repeated the calculations. At all altitudes a reduced rate coefficient results in slightly greater population ratios which persist for slightly longer times.

4. CONCLUSION

Treating the N_2 molecule as a harmonic oscillator and assuming that the only source of vibrational quanta arises from a nonthermal electron flux, we have calculated the N_2 vibrational distribution for an auroral model. During the auroral bombardment the N_2 vibrational distribution is non-Boltzmann with the lower levels underpopulated and the upper levels overpopulated relative to an energetically equivalent Boltzmann distribution. Above 200 km the non-Boltzmann distribution yields an O^+ loss rate which is 50 per cent greater than the rate obtained from the equivalent Boltzmann distribution. The population of the $C^3\pi_u$ state of N_2 has also been calculated and the results differed insignificantly from those obtained from the Boltzmann distribution.

REFERENCES

BAILEY, H. E. (1969). Numerical integration of the equations governing the one dimensional flow of a chemically reactive gas. *Physics Fluids* **12**, 2292–2300.
BELON, A. E., ROMICK, G. J. and REES, M. H. (1966). The energy spectrum of primary auroral electrons determined from auroral luminosity profiles. *Planet. Space Sci.* **14**, 597–615.

BENESCH, W., VANDERSLICE, J. T., TILFORD, S. G. and WILKINSON, P. G. (1966). Franck–Condon factors for observed transitions in N_2 above 6 ev. *Ap. J.* **143**, 236–252.

CHEN, J. C. Y. (1964). Theory of subexcitation electron scattering by molecules—II. Excitation and de-excitation of molecular vibration. *J. chem. Phys.* **40**, 3513–3520; **41**, 3263–3264.

DALGARNO, A., McELROY, M. B. and STEWART, A. I. (1969). Electron impact excitation of the dayglow. *J. atmos. Sci.* **26**, 753–762.

ENGELHARDT, A. G., PHELPS, A. V. and RISK, C. G. (1964). Determination of momentum transfer and inelastic collision cross sections for electrons in nitrogen using transport coefficients. *Phys. Rev.* **135**, A1566–A1574.

FISHER, E. R. and KUMMLER, R. H. (1968). Relaxation by vibration–vibration exchange processes. Part I. Pure gas case. *J. chem. Phys.* **49**, 1075–1084.

JACCHIA, L. G. (1964). Static diffusion models of the upper atmosphere with empirical temperature profiles. Res. in Space Sci., *Smithsonian Astrophys. Obs. Spec. Rpt.* **170**, 53.

RAPP, D. (1960). Complete classical theory of vibrational energy exchange. *J. chem. Phys.* **32**, 735–737.

RAPP, D. and ENGLANDER-GOLDEN, P. (1964). Resonant and near-resonant vibrational–vibrational energy transfer between molecules in collisions. *J. chem. Phys.* **40**, 573–575.

SCHMELTEKOPF, A. L., FERGUSON, E. E. and FEHSENFELD, F. C. (1968). Afterglow studies of the reactions He^+, $He(2^3S)$, and O^+ with vibrationally excited N_2. *J. chem. Phys.* **48**, 2966–2973.

SCHULZ, G. J. (1964). Vibrational excitation of N_2, CO, and H_2 by electron impact. *Phys. Rev.* **135**, A988–A994.

SHARP, T. E. and RAPP, D. (1965). Evaluation of approximations used in the calculation of excitation by collision—I. Vibrational excitation of molecules. *J. chem. Phys.* **43**, 1233–1244.

TREANOR, C. E., RICH, J. W. and REHM, R. G. (1968). Vibrational relaxation of anharmonic oscillators with exchange-dominated collisions. *J. chem. Phys.* **48**, 1798–1807.

WALKER, J. C. G. (1965). Analytic representation of upper atmosphere densities based on Jacchia's static diffusion models. *J. atmos. Sci.* **22**, 462–463.

WALKER, J. C. G. (1968). Electron and nitrogen vibrational temperatures in the E-region of the ionosphere. *Planet. Space Sci.* **16**, 321–327.

WALKER, J. C. G., STOLARSKI, R. S. and NAGY, A. F. (1969). The vibrational temperature of molecular nitrogen in the thermosphere. *Annls. Geophys.* **25**, 831–839.