

## THE EFFECT OF A SMALL AMOUNT OF O<sub>2</sub> ON VIBRATIONAL EXCITATION OF N<sub>2</sub>

ESMAIL JAMSHIDI

Chemical Engineering Institute, Tehran Polytechnic, Tehran (Iran)

(Received January 24, 1977)

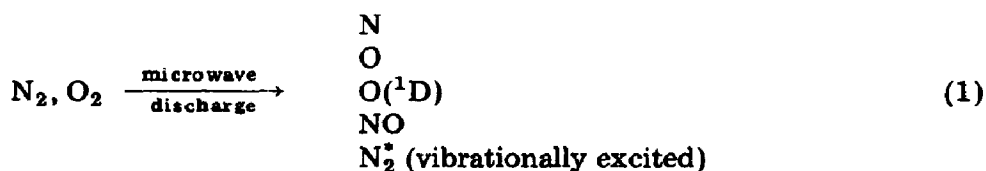
### Summary

It is well known that the vibrational temperature  $T_v$  is important in the measurement of some chemical rate constants (A.F. Schmeltekopf, F. Fehsenfeld, G. Gilman and E. Ferguson, Planet. Space Sci., 15 (1967) 401) and in high altitude chemistry. Since the lifetimes of many chemical reactions that depend on the  $T_v$  value of molecules are very short, it is desirable to produce a higher  $T_v$  from a given power source in order to have a good range of  $T_v$  for experiment. In this work it was found that adding a small amount of oxygen to a stream of nitrogen in a microwave discharge helped to produce a much higher  $T_v$  for N<sub>2</sub>. The vibrational temperature of N<sub>2</sub> is measured directly using an electron beam and indirectly using the vibrational-vibrational energy exchange of N<sub>2</sub> with CO and measuring the infrared radiation of CO. The measured values of  $T_v$  for N<sub>2</sub> with O<sub>2</sub> (3% of N<sub>2</sub>) and without O<sub>2</sub> were 1400 K and 700 K respectively.

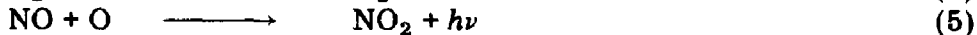
---

### 1. Chemical reactions

The work of Walker [1], Kummler *et al.* [2, 3], Varnum [4] and Jamshidi *et al.* [5] showed that some chemical species of oxygen are sources of vibrational excitation of nitrogen at high altitudes. In this experiment the same principle has been tested by adding a very small amount of oxygen to a stream of nitrogen in a microwave discharge. When a mixture of N<sub>2</sub> and a small amount of O<sub>2</sub> are passed through a microwave discharge several products result. For the purposes of this discussion, the important elements are the following:



Downstream from the discharge the following reactions could excite or de-excite the  $N_2$ :



Now let us consider each reaction separately.

(1) Since the amount of  $O_2$  is very small, we can assume that the effect of the  $O_2$  in reaction (1) on the excitation of  $N_2$  is negligible.

(2) It is well known that  $O(^1D)$  is rapidly quenched in collision with  $N_2$  [2, 3, 6]. There are 1.96 eV of energy available for the vibrational mode of  $N_2$ . If all available energy goes into the vibration of  $N_2$ , it can be excited up to the seventh vibrational level. Several theoretical and experimental investigations have been made which show the fraction of the available energy that is absorbed in the vibrational mode of  $N_2$  [7, 8]. However, the fraction of energy absorbed in the vibration of  $N_2$  is still not accurately known.

(3) Reaction (3) is exothermic by 3.25 eV and has a rate constant of  $2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  [9]. Early measurements showed that on average for effective collision of N and NO,  $N_2^*$  ( $v = 3$ ) excited to the third vibrational level is produced [10]. Later measurements indicated both stronger and weaker coupling. On average we could assume that  $N_2^*$  can be excited up to the fourth vibrational level.

(4) Measurements by Breshears and Bird [11] at high temperature ( $T = 2000 \text{ K}$ ) and McNeal *et al.* [12] show that the oxygen atoms can de-excite  $N_2^*$ . This reaction can play an important role in relaxing the  $N_2^*$  when enough atomic oxygen is present. The rate constant  $k = 1 \times 10^{-13} \times \exp(-23/T^{-1/3})$  can be derived from the experimental work of McNeal *et al.* [12]. Over all the relaxation of  $N_2^*$  with atomic oxygen is much faster than the relaxation rate with oxygen molecules.

(5) Reaction (5) does not play an important role in the excitation of  $N_2^*$ . The glow of emitted light is visible at the initial stage of interactions, which is a good indication of the presence of NO and O atoms.

(6) The effect of wall deactivation and of other gases such as inert carrier gases on  $N_2$  are the same with or without the small amount of oxygen, except when these interact with oxygen or its derivatives.

## 2. Experimental procedure

Nitrogen is introduced into a quartz tube (internal diameter 1 cm) where it can be vibrationally excited using a microwave discharge cavity at 2450 MHz. The excited  $N_2^*$  (Fig. 1) enters a stainless steel tube (flow tube) (internal diameter, 5 cm) at one of windows 1, 2, 3, 4, 5 or 6. The choice of window depends on the velocity of the flow and the time required for the mixture of  $O_2$  and  $N_2$  to reach window 7. At window 7 a beam of electrons

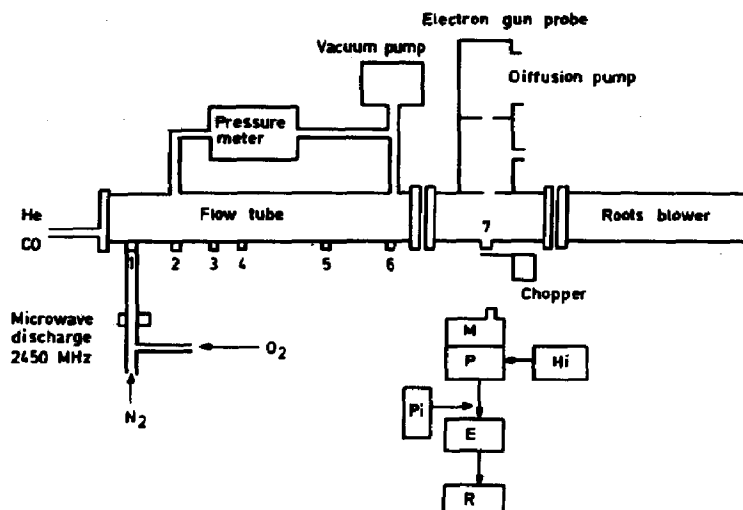


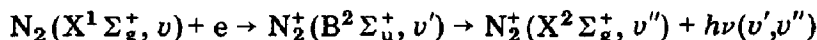
Fig. 1. The flow tube reactor and detection system.

is introduced perpendicular to the flow of gases. The electron beam is produced using a welding electron gun (Model 281-1SS, Brad Thompson Industries) with power supply 1 617 (Brad Thompson Industries) at pressures less than  $10^{-4}$  Torr. This pressure is reached using two diffusion pumps (DW 200 and DW100, Vacuum Instrument Corporation) with pumping speeds of 600 and  $300 \text{ l s}^{-1}$  in a differentially pumped system.

The ultraviolet light emitted from the interaction of the electron beam and the flow of gases is detected through window 7 (Infrasil with thickness 0.5 cm and diameter 2.2 cm; Muffoletto Optical Company Inc.) using a lens ( $\text{BaF}_2$  with diameter 2.5 cm and focal length 5 cm) to focus on a Jarrell-Ash 82-410 quarter-meter monochromator, measured by a photomultiplier with a 244 high voltage supply (Keighley Instruments) and a 261 pA source (Keighley Instruments) and recorded with a 194 Honeywell recorder.

### 3. Measurement of the $\text{N}_2^+$ vibrational temperature

Vibrationally excited nitrogen interacts with a high energy electron beam (19 kV) as follows:



The emitted light is a function of  $v'$  and  $v''$ . (The wavelengths are given by Tyte and Nichols [13].)

The distribution of  $\text{N}_2^+(\text{B})$  amongst the vibrational levels  $v'$  is a function of the Franck-Condon factor  $q_{v', v''}$  and the distribution of  $\text{N}_2(\text{X})$  over  $v$  levels, or  $\text{N}_2^+(\text{B}, v') \approx \sum q_{v', v''} \text{N}_2(\text{X}, v)$ .

The intensity of emitted light at wavelengths corresponding to  $\text{N}_2^+(\text{B}, v') \rightarrow \text{N}_2^+(\text{X}, v'')$  is a function of the radiative lifetime, the population density of

$N_2^+(B)$  at level  $v'$  and the Franck-Condon factor for the transition from  $N_2^+(B)$  to  $N_2^+(X)$ . Knowing all of these parameters one can calculate the intensity of the emitted light for different transitions. The method is described by Schmeltekopf *et al.* [14]. They plotted (Fig. 2) the population density of  $N_2^+(B)$ , which is directly proportional to the emission intensity, versus the vibrational temperature. Transitions  $N_2^+(B, v' = 0) \rightarrow N_2^+(X, v'' = 0)$  and  $N_2^+(B, v' = 0) \rightarrow N_2^+(X, v'' = 1)$  emit light at 3914.5 and 4278 Å, respectively. At higher vibrational temperatures  $T_v$  of  $N_2(X)$  the relative population of  $N_2^+(B, v' = 0)$  decreases and the relative population of  $N_2^+(B, v' \geq 1)$  increases. Therefore, the intensity of the emitted light at 3914.5 Å and 4278 Å changes. These changes in intensity of emitted light can be correlated to the  $T_v$  of  $N_2(X)$ . The decrease in intensity of  $N_2^+(B, v' = 0)$  can also be the result of the

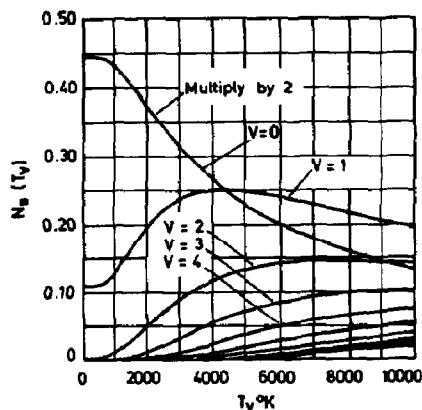


Fig. 2. Relative number density of  $N_2^+(B)$  vs. vibrational temperature of  $N_2(X)$ . (From Schmeltekopf *et al.* [14].)

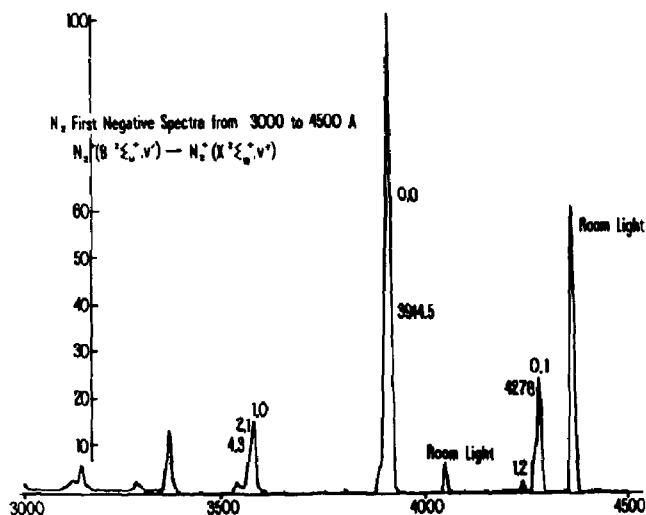
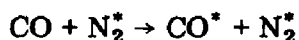


Fig. 3. Spectra of pure  $N_2$  when interacted with an electron beam. The numbers on the peaks show the vibrational transition from  $v'$  to  $v''$ .

dissociation of  $N_2$  or the reaction of  $N_2$  with  $O_2$ . Therefore, it is better to use a transition such as  $N_2^+(B, v' \geq 1)$  or another method to ensure the excitation of  $N_2^+$ . The spectrum of  $N_2^+$  when it has interacted with an electron beam is shown in Fig. 3, where it can be seen that the highest peak for low  $T_v$  of  $N_2^+$  belongs to the  $N_2^+(B, v' = 0)$  transitions. Since the other transitions such as  $N_2^+(B, v' \geq 1)$  are low in intensity and close to each other, a monochromator with higher resolution is required.

In order to show that any change in the intensity of the  $N_2^+(B, v = 0)$  transitions is not the result of a chemical reaction of  $N_2$ , the IR radiation of vibrationally excited carbon monoxide is used. The IR spectrum of CO is due to the vibrational excitation of CO in the reaction



Since the vibration-vibration (V-V) energy exchange between CO and  $N_2$  is very rapid compared with the vibrational-translational (V-T) energy exchange, the quasi-steady state of V-V equilibrium should follow the relation due to Treanor *et al.* [15].

#### 4. Results

With low pressure of nitrogen gas (0.1 - 1.0 Torr) it was possible to excite  $N_2$  to a vibrational temperature of up to 2000 K, which is a desirable range for most experimental studies. When the pressure of  $N_2$  was increased to 3 Torr, however, the  $T_v$  of  $N_2$  decreased to 700 K. 0.1 Torr of  $O_2$  gas was added to the stream of 3 Torr  $N_2$ . In order to measure the  $T_v$  of  $N_2$  and to avoid the necessity of considering the interaction of  $O_2$  and  $N_2$  (which could result in a reduction of the intensity of  $N_2^+(B)$ ) 0.1 Torr of CO and He (He to keep the total pressure constant) was introduced into the flow tube and mixed with the  $N_2$  and  $O_2$  stream. Figure 4 shows the effect of CO on the  $N_2^+(B, v' = 0) \rightarrow N_2^+(X, v'' = 0)$  transition when the concentration of CO is more than that of  $N_2$ . It demonstrates that the effect of CO is negligible in this transition. Therefore this transition can be used to measure the  $T_v$  of  $N_2$ . The effect of switching the microwave discharge on and off on the spectra of  $N_2 + CO$  (see Fig. 5) indicates a substantial change in the emission of  $N_2^+(B, v' = 0)$  to  $N_2^+(X, v'' = 0)$  and  $N_2^+(X, v'' = 1)$ . For the final measurement the monochromator was set to a wavelength of 3914.5 Å and then 3 Torr of  $N_2$  and 0.1 Torr of  $O_2$  were discharged. The discharged gas was introduced into the flow tube and mixed with a 0.11 Torr mixture of He + CO downstream from the discharge. After 13 ms the mixture interacted with an electron beam. The emitted light was detected at 3914.5 Å. By turning the microwave discharge on and off (Fig. 6) and using Fig. 2 the  $T_v$  of  $N_2$  was calculated. The measured  $T_v$  of  $N_2$  averages 1300 K, compared with the  $T_v$  of  $N_2$  without the small addition of oxygen which was 700 K. Since the addition of a small amount of oxygen almost doubled the  $T_v$  of  $N_2$ , this can be considered a good method for increasing the  $T_v$  of  $N_2$ . As mentioned previously, the IR

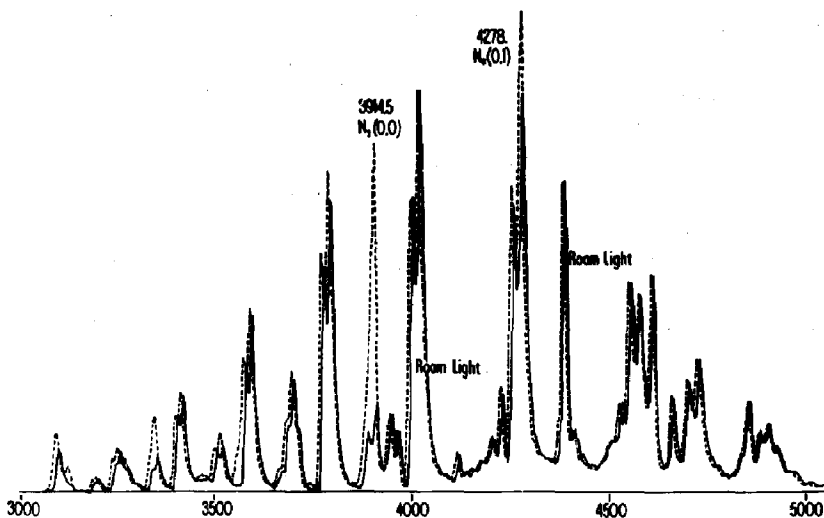


Fig. 4. The effect of CO on the spectra of  $N_2 + CO$ : solid curve, CO emission spectrum excited by 17 kV electrons; broken curve,  $CO + N_2$  emission spectrum excited by 17 kV electrons.

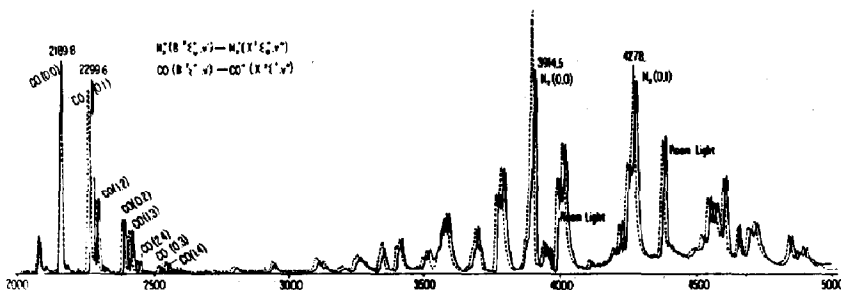


Fig. 5. The effect of discharge on the spectra of the  $N_2$  and CO mixture at pressures of 20 and 110  $\mu m$  respectively: solid curve, discharged  $N_2 + CO$ ; broken curve, cold  $N_2 + CO$ .

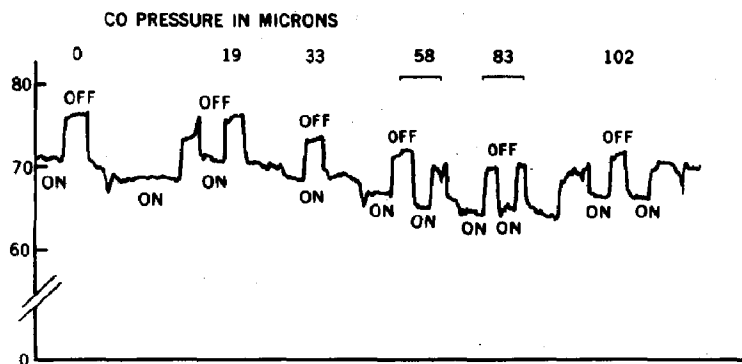


Fig. 6. The effect of the discharge on the emission from  $N_2^+(B)$  at 3914.5  $\text{\AA}$  when 3 Torr of  $N_2$  and 100  $\mu m$  of  $O_2$  are subjected to a discharge and are then mixed with CO.

radiation of CO which is excited by  $N_2$  can provide a good indication of the  $T_v$  of  $N_2$  [15, 16]. Since the reaction lifetime for the V-V energy exchange between CO and  $N_2$  with  $k = 461 \text{ Torr}^{-1} \text{ s}^{-1}$  [17] is about 9 ms (which is less than the reaction residence time of 13 ms) it can be assumed that there is a quasi-equilibrium [18] in V-V energy exchange between CO and  $N_2$ . During this equilibrium the Treanor relation holds.

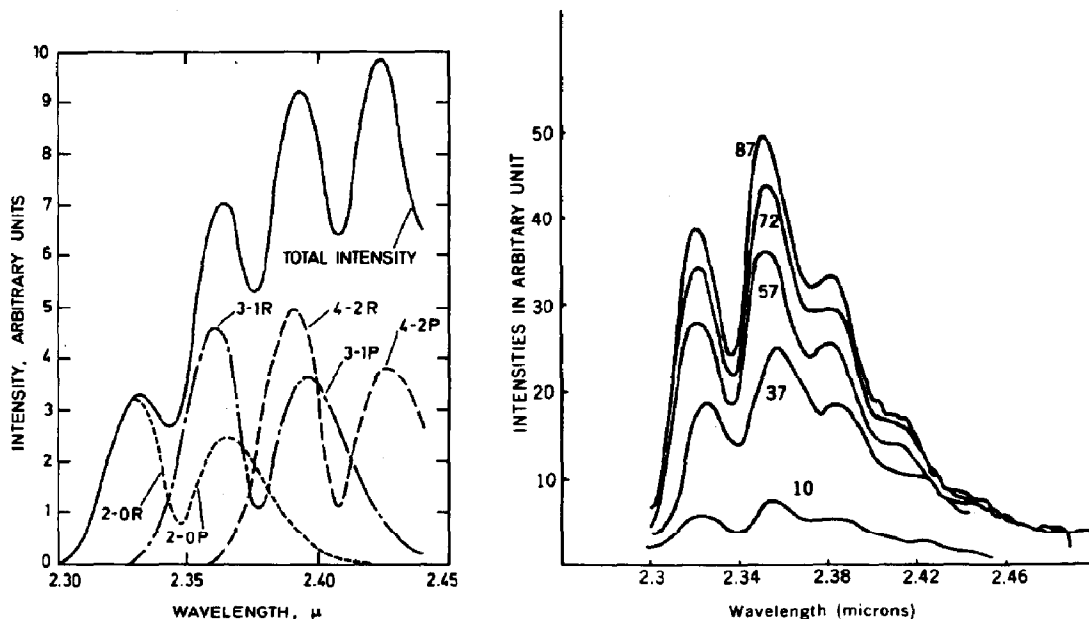


Fig. 7. The effect of overlap on the low resolution CO first overtone band profile. (From Horn *et al.* [19].)

Fig. 8. Infrared radiation of CO, when mixed with excited  $N_2 + O_2$ :  $P_{N_2} = 3000 \mu\text{m}$ ;  $P_{O_2} = 100 \mu\text{m}$ ;  $P_{CO}$  values (in  $\mu\text{m}$ ) are indicated on the curves;  $T_v$  of  $N_2 \approx 1300 \text{ K}$ ; full scale sensitivity of the amplifier,  $100 \mu\text{V}$ .

The vibrational temperature of CO is measured using a CO first overtone band profile which is presented in Fig. 7 [19] and a computer program to fit the total intensity [20]. The IR spectrum of  $CO^*$  which is excited by  $N_2$  is shown in Fig. 8 and the calculated  $T_v$  of CO using the first six peaks to fit the total intensity are shown in Table 1 where the  $T_v$  of CO varies from 1752 to 1895 K for different concentrations of CO. The IR radiation of  $CO^*$  takes some vibrational energy from  $N_2^*$ . As CO concentration increases, more vibrational energy is taken from  $N_2^*$ . Therefore, there will be some decline in the  $T_v$  of  $N_2^*$  and  $CO^*$  as the CO concentration increases.

TABLE 1

The first six peaks of the IR spectra of CO when it is mixed with 3000  $\mu\text{m}$   $\text{N}_2$  with  $T_v(\text{N}_2) = 1300$  K

$P_{\text{CO}}$ ( $\mu\text{m}$ )	Full scale/ time constant ( $\mu\text{V/s}$ )	Intensity at the peak number						$T_v$ of CO (K)	$\Sigma (I - I_F)$
		1	2	3	4	5	6		
10	20/3	21.5	31.5	22	13	6	2.5	1895	0.76
10	50/3	10	14	10	57	3	2	1923	0.24
37	50/3	35.3	47	33	18.5	9	5	1844	1.8
57	50/3	52	67	46	26	12	5.5	1795	4.0
57	100/1	27	36.5	25	14	7	4	1849	1.3
72	100/1	33.8	43.3	29	16	7.6	4	1772	2.5
87	100/1	38.2	4.9	33	17	8.4	4.5	1752	2.6

$I_F$ , fitted intensity.

## 5. Conclusion

Adding 0.1 Torr of oxygen gas to 3 Torr nitrogen gas in a microwave discharge increased the  $T_v$  of  $\text{N}_2^+$  from 700 K to 1300 K, where the  $T_v$  of  $\text{N}_2^+$  was measured using the direct method, the transition of  $\text{N}_2^+(\text{B}, v' = 0) \rightarrow \text{N}_2^+(\text{X}, v'' = 0)$  and the indirect methods of the Treanor relation and the  $T_v$  of CO (the  $T_v$  of CO was measured using the IR radiation of CO). Increasing the  $T_v$  of  $\text{N}_2$  by almost a factor of 2 just by adding a small amount of  $\text{O}_2$  can be considered a good improvement.

Some chemical reactions were proposed which could be responsible for the increase in the  $T_v$  of  $\text{N}_2$ . More detailed work which measures possible chemical elements derived from  $\text{N}_2$  and  $\text{O}_2$  discharges, chemical reaction rate constants, and electronic-vibrational and vibration-vibration energy exchange between them is needed in order to calculate the optimum fraction of  $\text{O}_2$  which should be added to obtain the desired  $T_v$  of  $\text{N}_2$ .

## References

- 1 J. Walker, Electron and  $\text{N}_2$  vibrational temperature in the E region of the ionosphere, *Planet. Space Sci.*, 16 (1968) 321.
- 2 R. Kummler and M. Bortner, Vibrational temperature in the E and F regions, *Space Res.*, 12 (1972) 711.
- 3 R. Kummler, F. Gilmore and J. W. McGowan, Excitation-de-excitation processes. In M. Bortner and T. Baurer (eds.), *DNA Reaction Rate Handbook* (2nd edn.), DNA-1948H, General Electric Tempo, Santa Barbara, Calif., 1972.
- 4 W. Varnum, Enhanced  $\text{N}_2$  vibrational temperatures in the thermosphere, *Planet. Space Sci.*, 20 (1972) 1865.
- 5 E. Jamshidi, E. R. Fisher and R. Kummler, Vibration temperature of  $\text{N}_2$  in the E and F regions, *J. Geophys. Res.*, 87 (27) (1973).
- 6 E. Zipf, The collisional deactivation of metastable atoms and molecules in the upper



- atmosphere, *Can. J. Chem.* 27 (1969) 1863.
- 7 E. Bauer, E. Fisher and F. Gilmore, De-excitation of electronically excited sodium by nitrogen, *J. Chem. Phys.*, 51 (1969) 4173.
  - 8 E. Fisher and E. Bauer, On the quenching of  $O(^1D)$  by  $N_2$  and related reactions, *J. Chem. Phys.*, 57 (1972) 1966.
  - 9 M. Bortner and R. Kummeler, The revision of the DASA reaction rate handbook and supporting analytical and experimental work designed for its improved application, DASA Rep. 2407, General Electric Space Science Laboratory, Valley Forge, Pa., 1970.
  - 10 J. Morgan, L. Phillips and H. Schiff, Studies of vibrationally excited nitrogen using mass spectrometer, and calorimeter-probe techniques, *Discuss. Faraday Soc.*, 33 (1962) 118.
  - 11 W. Breshears and R. Bird, Effect of oxygen atoms on the vibrational-relaxation of nitrogen, *J. Chem. Phys.*, 48 (1968) 4768.
  - 12 R. McNeal, M. Whitson, Jr., and C. Cook, Quenching of vibrationally excited  $N_2$  by atomic oxygen, *Chem. Phys. Lett.*, 16 (1972) 507.
  - 13 D. C. Tyte and R. W. Nichols, The  $N_2^+ B^2 \Sigma_u^+ - X^2 \Sigma^+$  first negative system of  $N_2$ , Rep. No. NASA-CR-74950, NASA Accession No. N66-25320, 1965.
  - 14 A. Schmeltekopf, E. Ferguson and F. Fehsenfeld, Afterflow studies of the reactions of  $He^+$ ,  $He(2^3S)$  and  $O^+$  with vibrationally excited  $N_2$ , *J. Chem. Phys.*, 48 (1968) 2966.
  - 15 C. Treanor, J. W. Rich and R. G. Rehm, *J. Chem. Phys.*, 48 (1968) 1798.
  - 16 E. Jamshidi and R. Kummeler, Experimental proof of Treanor relation, 2nd Congr. of Chemical Engineering, Tehran, May 1974.
  - 17 P. F. Zittel and C. B. Moore, Rate constant of vibration-to-vibration energy transfer in  $N_2CO$ , *Appl. Phys. Lett.*, 21 (3) (1972).
  - 18 G. Abraham and E. R. Fisher, Modeling of a pulsed  $CO/N_2$  molecular laser system, *J. Appl. Phys.*, 43 (11) (1972).
  - 19 K. P. Horn and P. E. Oettinger, Vibration energy transfer in  $N_2^+ - CO$  and  $N_2 - NO$  mixtures, Aerospace Rep. No. TR-0059 (6220-50), 1970.
  - 20 A. Lightman, personal communication.