EXCITATION MECHANISMS OF THE PULSED DISCHARGE NITROGEN GAS LASER

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The excitation processes involved in bringing about population inversions and laser action in nitrogen have been discussed. The two processes advocated in literature are: (*a*) the indirect excitation process of Mathias and Parker, and (*b*) by direct electron impact. On the basis of available evidence, the second process appears more probable. Certain laser transitions in the first positive system of nitrogen dominate and suppress other weaker transitions. This dominance is explained on the basis of direct electron impact excitation.

INTRODUCTION

The pulsed nitrogen gas laser was the first molecular laser to be discovered and has been studied by quite a few researchers with a view to understanding the excitation mechanisms involved. Two models have been put forward as the possible processes bringing about the population inversion. They are the indirect excitation model of Mathias and Parker (1963) and direct excitation by electron impact suggested by Cheo and Cooper (1964).

THE INDIRECT EXCITATION MODEL

In the indirect process, suggested by Mathias and Parker, electron impact with the ground state molecules produces molecules in the $a^1\Pi_g$ state

$$X^1\Sigma_g^+ + e \rightarrow a^1\Pi_g + e \quad .. \quad .. \quad .. \quad .. \quad (1)$$

collisions between $a^1\Pi_g$ and $X^1\Sigma_g^+$ were thought to produce the $B^3\Pi_g$ state

$$a^1\Pi_g + X^1\Sigma_g^+ \rightarrow B^3\Pi_g + X^1\Sigma_g^+ + E \quad .. \quad .. \quad (2)$$

The possibility of direct excitation from $X^1\Sigma_g^+$ to $B^3\Pi_g$ was ruled out because it represented a singlet to triplet excitation and hence violated selection rules. This, however, overlooks the forbidden nature of the g–g transition for $X^1\Sigma_g^+ \rightarrow a^1\Pi_g$.

Now the rate of the collisional transfer process suggested by Mathias will be governed by gas collision frequencies and the time delay between collisions is of the order of 10^{-7} sec. (McDaniel 1964). Hence one would expect the spontaneous delay time, which is the time between the start of the current pulse and start of the spontaneous emission to be of about this magnitude. Experimental studies made on the nitrogen laser (Sivaram 1968) suggest that there is no measurable time delay between the current pulse and the spontaneous emission from the discharge tube.

The other conditions to be satisfied (Heath 1959) for collisional transfers to have reasonable cross-sections are:

(*a*) The energy difference between the two states involved in the collision should be negligibly small, and little or no energy must be changed into or received from translatory motion. The lowest vibrational state energies of the $a^1\Pi_g$ and $B^3\Pi_g$ states are 69290 cm^{-1} and 59626 cm^{-1} respectively—a difference of 9664 cm^{-1} (Herzberg 1950).

(*b*) The spin conservation rule of Wigner states that there is a preference for an energy transfer to take place if the total resultant electronic spin of the colliding species remains unchanged during the collision. For the reaction

$$a^1\Pi_g + X^1\Sigma_g^+ \rightarrow B^3\Pi_g + X^1\Sigma_g^+$$

spin is not conserved.

(*c*) If an electronic state in a molecule is excited or de-excited there are certain restrictions imposed on these processes by the Franck-Condon principle. This principle states that during a transition involving an electronic state of the molecule, the transition takes place so rapidly in comparison to the vibrational motion that immediately after the transition the nuclei have very nearly the same relative position and velocity as before. Thus during the transition the equilibrium internuclear distance R_e remains almost unchanged. In effect the molecule will tend to go into a state where R_e is very nearly the same as before. R_e values for some of the relevant states of nitrogen are as given below (Herzberg 1950):

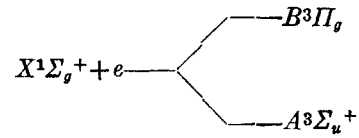
State	R_e (Å)	*Energy* (cm^{-1})
$X^1\Sigma_g^+$	1·094	0
$a^1\Pi_g$	1·213	69290
$A^3\Sigma_u^+$	1·293	50206
$B^3\Pi_g$	1·212	59626
$C^3\Pi_u$	1·148	89147

R_e is almost the same for the $B^3\Pi_g$ and $a^1\Pi_g$ states. Hence in equation 2, R_e *does not change appreciably.* But in equation 1 the equilibrium internuclear distance is altered considerably.

If equations 1 and 2 represent the mechanism for populating the $B^3\Pi_g$ state and achieving population inversion in the first positive system, then high population densities of $a^1\Pi_g$ should occur in the discharge. Spontaneous emission from $a^1\Pi_g$ to the ground level should be easily noticeable. The spectrograms of the spontaneous emission under pulsed excitation (Sivaram 1968) showed no evidence of the Lyman Birge Hopfield System, $a^1\Pi_g \rightarrow X^1\Sigma_g^+$.

The Direct Excitation Model

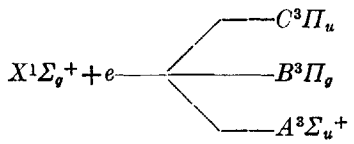
The direct excitation process suggested by Cheo and Cooper (1964) is as below:



(3)

A singlet to triplet excitation is possible with a fairly large but sharply defined probability. The incident electron may be considered to have replaced one of the valence electrons during the collision and to have its spin parallel to that of the other valence electron.

In equation 3 also, the dipole selection rules are not obeyed, for excitation to the A and B states. Gerry (1965) assumed direct excitation to the B and C states to explain the observed super-radiance in the nitrogen second positive system. The $C^3\Pi_u$ state was quoted as having a ten times larger excitation cross-section than the $B^3\Pi_g$ state. Thus the excitation process can be written as:



(4)

On the basis of the Franck-Condon principle, the $C^3\Pi_u$ state involves the smallest change in R_e and hence would have the largest value of the Franck-Condon factor. The next most easily excitable states would be the $B^3\Pi_g$, $a^1\Pi_g$ and $A^3\Sigma_u^+$. The excitation cross-sections for electron impact are proportional to the Franck-Condon factor and to [const—log $(E_n - E_0)$] where E_n and E_0 are the excited and ground state energies (Hasted 1964). Because of the log $(E_n - E_0)$ term the cross-section for $a^1\Pi_g$ will be smaller than for $B^3\Pi_g$ even though they have almost the same value of R_e and hence almost identical Franck-Condon factors. It is these differences in the values of the Franck-Condon factors which cause the observed population inversions between $C^3\Pi_u$ and $B^3\Pi_g$ states and between $B^3\Pi_g$ and $A^3\Sigma_u^+$ states, when nitrogen is excited by electron impact.

The population of the vibrational levels of $B^3\Pi_g$ in the first positive laser show a variation with the quantum number v which is similar to that anticipated on the basis of the Franck-Condon principle. Kasuya and Lide (1967) give the relative populations of the vibrational levels of the $B^3\Pi_g$ state, as in Table I.

The Franck-Condon factor or overlap integral involves the vibrational wave functions and is of the form $\phi_1(v_1) \cdot \phi_2(v_2)$. Different vibrational bands have different values of ϕ and hence the observed population distributions in

the vibrational levels. The indirect excitation model fails to explain this distribution of population. The direct excitation mechanism is also able to explain the large population in the $v = 0$ level of the second positive laser. Jobe *et al.* (1967) have measured the relative values of the maximum excitation cross-section for the $v = 0$, 1 and 2 vibrational levels as 25·4, 18·6 and 7·9 respectively, for electron impact excitation, and find it conforms with the distribution expected on the basis of the Franck-Condon principle.

TABLE I

Relative populations in vibrational levels of $B^3\Pi_g$ state

v	Relative population N
0	0·096
1	0·481
2	0·923
3	0·545
4	0·345

The delay times of the U.V. laser and I.R. laser are both very small (Sivaram 1968). For a 4 mm diameter laser tube $(T_d)_{\text{U.V.}} = 0{\cdot}03$ μ secs. and $(T_d)_{\text{I.R.}} = 0{\cdot}10$ μ secs. This time sequence is due to the electron energy distribution in the current pulse, the high energy electrons occurring in the initial portion of the current pulse, when the voltage is high. This coupled with a ten times larger value of excitation cross-section for the $C^3\Pi_u$ state than for the $B^3\Pi_g$ state causes the U.V. laser to oscillate before the I.R. laser. This dependence on the electron energies and densities lends support to the direct impact hypothesis.

It thus appears that the population inversion processes in the nitrogen first and second positive systems are due to excitation by electron impact with the ground state—the excitation cross-sections being governed by the Franck-Condon principle.

The validity of this conclusion can be tested by applying it to the CO laser (Mathias and Parker 1963) which is isoelectronic with N_2. The CO laser works on the Angstrom band system $B^1\Sigma$–$A^1\Pi$ and the ground state is $X^1\Sigma^+$. The values of R_e, the internuclear distances, are as below (Herzberg 1950):

State	R_e (Å)
$B^1\Sigma^+$	1·120
$A^1\Pi$	1·2351
$X^1\Sigma^+$	1·1281

This suggests that the $B^1\Sigma^+$ state will have the higher Franck-Condon factor and hence higher excitation cross-sections compared to $A^1\Pi$. Hence the population inversion is expected to, and indeed it does, occur between $B^1\Sigma^+$ and $A^1\Pi$ states.

Interactions in the I.R. System

Figure (1) indicates diagrammatically some of the strong laser transitions of the Q_1 branch observed in the first positive system of nitrogen. The laser lines Q_1–5 to Q_1–9 of the (1, 0) band have common lower levels with corresponding lines in the (0, 0) band. The lines of the (0, 1) band have common upper levels with the corresponding lines in the (0, 0) band. The (0, 1) band lines again have common lower levels with the (2, 1) band lines. Thus the various bands including (2, 0), (3, 1), etc., interact with each other. In a study of the nitrogen laser (Sivaram 1968), I.R. dielectric mirrors coated at 7753 Å were used and only the (1, 0) and (2, 1) band lines were observed. The reasons for this are as follows:

For low repetition frequencies, one can neglect the lower level population and the gain G of the laser is given by ($G = C \times N_v \times$ Band strength $\times$ Hönl-London factor) where N_v = upper level population and C is a constant. The Hönl-London factors are largest for the Q_1 branch and increase linearly with K. The peak gain occurs for the Q_1–9 lines and this is because of the nature of the population distribution in the rotational levels. The maximum population occurs in the $K = 9$ level for a rotational temperature of about 320 °K (Kasuya and Lide 1967). This value of K_{max} remains the same for the various vibrational bands. This is because, in excitation by electron collision, no great change in the angular momentum of the system can be produced (owing to the smallness of the electron mass) and therefore the relative distribution of the molecules over the different rotational levels in the upper electronic state is practically the same as in the ground state (Herzberg 1950). The actual number densities in any rotational level will, however, be different for the various vibrational levels, and will be governed by the Franck-Condon principle. The relative populations of the $v = 1$, 2, 3 and 4 vibrational levels of the $B^3\Pi_g$ state are as quoted earlier in Table I.

The band strengths of these bands (Nicholls 1964) are given in Table II. The gain depends on the product $P = N \times$ Band strength; because, if only a single rotational line is considered, the Hönl-London factor will remain constant. The value of P for the various known laser bands are as in Table III. Thus the gain is highest for the (1, 0) band and is followed by the (2, 1) band. The other bands have much lower gain. Even though the mirror reflectivities were peaked around 7753 Å for the (2, 0) band, the residual reflectivities at 8700 and 8900 Å were still high enough to sustain oscillation on the high

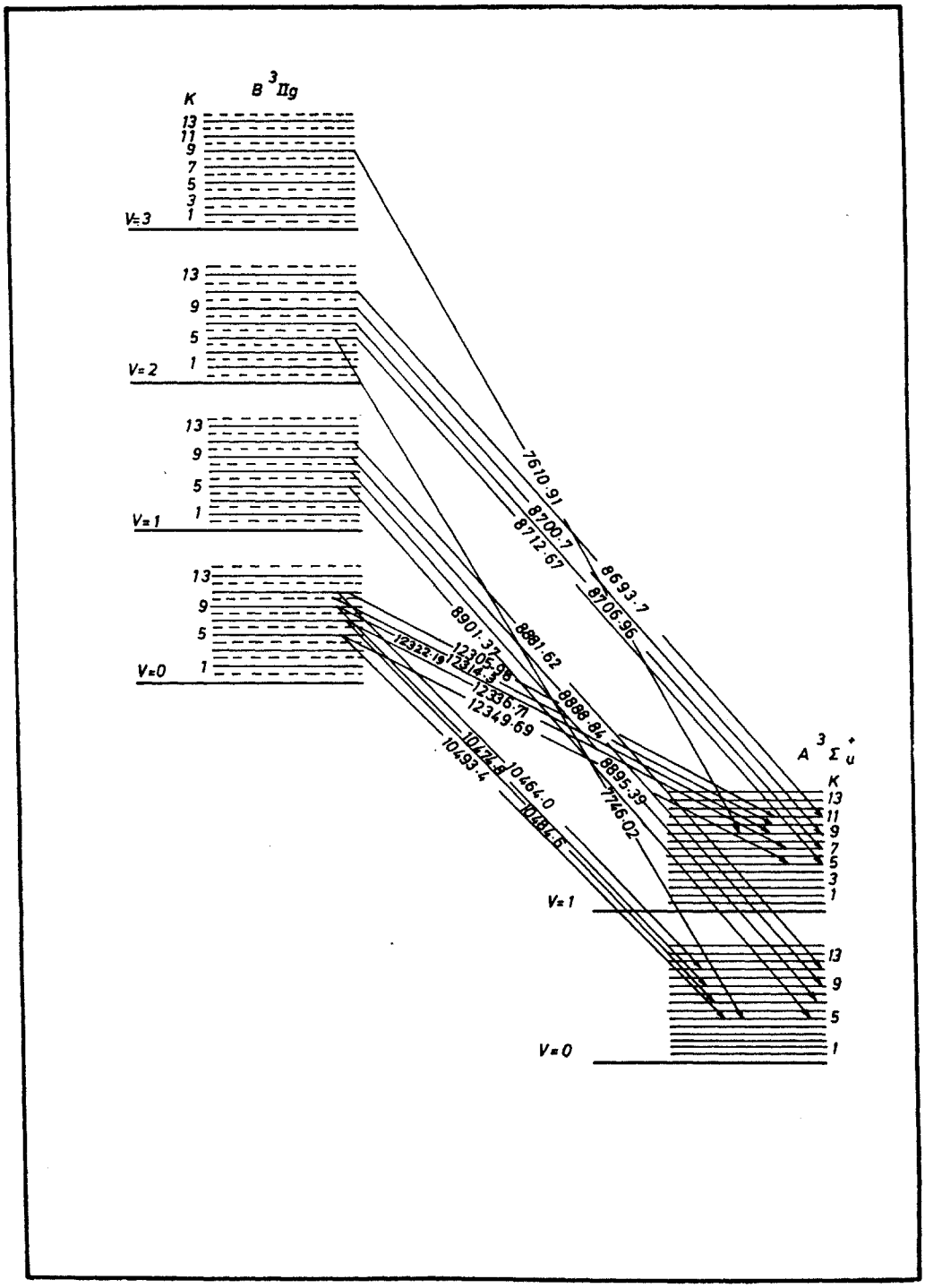


FIG. 1. Interactions in the N_2 laser.

gain (1, 0) and (2, 1) bands (Sivaram 1968). The build up of oscillation on these two bands quenches the population inversion in the (2, 0) band by draining the upper level and filling up the lower level. The (2, 1) and (1, 0) bands also populate the lower levels of the (0, 1) and (0, 0) bands respectively,

TABLE II

Band strengths for some bands of the N_2 first positive system

Band	Wavelength Å	Band strength $a_0^2e^2x\ 10^{-1}$
0, 0	10387	2·82
0, 1	12211	3·27
1, 0	8851	2·62
2, 0	7694	0·957
2, 1	8673	1·310
3, 1	7569	1·38
4, 2	7451	1·20

TABLE III

Band	$P(a_0^2e^2)$
0, 1	0·314
0, 0	0·271
1, 0	1·260
2, 0	0·883
2, 1	1·209
3, 1	0·752
4, 2	0·415

and hence oscillation appears to be unlikely on these bands. These bands can be observed if the (1, 0) and (2, 1) bands are suppressed from oscillation by means of a prism in the cavity and using suitable mirrors. The (2, 0) band lines at 7746 Å were observed (Sivaram 1968) in laser emission by using He-Ne laser mirrors, coated for 6328 Å, and Knyazev (1966) used an intracavity prism to suppress the strong laser bands and got the weaker ones to oscillate. It thus appears that direct excitation by electron impact is the predominant mechanism producing the observed population inversions in the nitrogen gas laser.

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