Relative reaction rates in rotational and vibrational excitation of \( \text{N}_2(\text{C} \, 3\Pi_u) \) by \( \text{Ar}^*(3P_0) \) and \( \text{Ar}^*(3P_2) \) metastable atoms

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RELATIVE REACTION RATES IN ROTATIONAL AND VIBRATIONAL EXCITATION OF N₂(C²Πₐ) BY Ar*(3P₀) AND Ar*(3P₂) METASTABLE ATOMS

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Résumé. — Le transfert d’excitation entre Ar(3P₀), Ar(3P₂) et molécules d’azote est étudié par la technique de post-décharge. D’une part, la décroissance des populations des atomes métastables d’argon est comparée à celle des intensités des bandes d’émission du système second positif de N₂. D’autre part, une perturbation sélective est réalisée sur l’un des niveaux Ar(3P₀), Ar(3P₂) par la technique de pompage optique utilisant un laser à colorant accordable ; les variations relatives obtenues sur l’intensité des bandes d’émission de N₂ ont permis de déterminer le rapport des coefficients de réaction de transfert d’excitation vibrationnelle et rotationnelle de N₂(C²Πₐ) par Ar(3P₀) et Ar(3P₂).

Abstract. — The energy transfer reaction between Ar(3P₀), Ar(3P₂) and molecules of N₂ was studied in the afterglow of a pulsed electrodeless discharge. The population decays of the metastable argon atoms and the intensity decays of the nitrogen second positive emission bands were monitored simultaneously. A dye laser was used to selectively depopulate each metastable argon species and the relative variations were checked on the intensity of the nitrogen second positive bands. Relative reaction rates in rotational and vibrational excitation of N₂(C²Πₐ) by Ar(3P₀) and Ar(3P₂) were obtained.

1. Introduction. — The energy transfer by collisions between excited argon atoms in the (3p⁵ 4s) levels and nitrogen molecules has been a subject of repeated investigations during the last few years ([1] to [7]). This is related not only to its fundamental importance in understanding the energy transfer processes in general but also in relation to the electron beam excited Ar-N₂ laser for which the specific contribution of each excited argon level to the population inversion are not well known. It has generally been accepted in previous investigations that the whole populations of the argon 3p⁵ 4s levels, usually designated by 3P₂, 3P₁, 3P₀ and 1P₁, participate in the excitation transfer leading to the formation of the excited state N₂(C²Πₐ).

Numerous results have been obtained in these early studies. However, some controversies remain, for example it is not clear whether the collision transfer process involves complex formation, in which case the observed first positive band N₂(B²Π₈ → A²Σ₊) is explained [1], or if it involves direct Frank-Condon excitation [6]. Furthermore, excepting Chen et al. [7], no attempt was made in previous studies to determine the specific contribution of each argon atom species in the transfer. For this purpose a program of experiments is at present under way in our laboratory with the aim of specifying the efficiency of each energy donor state argon 3P₂, 3P₁, 3P₀ and 1P₁ in the formation of the N₂(C²Πₐ, v', K') level in each vibrational and rotational state. In the present paper we report the first experimental results concerning the relative values of the coefficient rates for the production of N₂(C²Πₐ, v', K') by argon 3P₂ and 3P₀ metastable atoms.

The experiment was performed in the late afterglow where the populations of the 3P₁ and 1P₁ levels were very weak and we have verified that their contribution to the energy transfer can be neglected compared to that of Ar(3P₂) and Ar(3P₀). We used the stationary afterglow technique in a HF pulsed electrodeless discharge applied to a Ar : N₂ = 1 000 : 1 gas mixture at the total pressure of about 0.2 torr and contained in a quartz cylindrical cell (diameter = 7 cm ; length = 30 cm).

This technique provided the observation of N₂(C²Πₐ) produced only by transfer from argon metastables. The time dependence study associated with an original perturbation method based on the
optical pumping technique, utilizing a tunable dye laser, was used. It enables one of the metastable argon levels to be selectively depopulated and simultaneously provides a check of the relative variation of the population of each excited N$_2$(C $^3$II$_u$, v', K') level.

2. Experiment. — The major part of our experimental system has already been described in detail elsewhere [8]. We report here briefly pertinent features. A weak pressure (≈ 0.2 torr) was used in order (1) to avoid the rotational relaxation of N$_2$(C $^3$II$_u$, v', K') molecules before radiative emission, (2) to ensure lower quenching efficiency of both metastable atoms and N$_2$(C $^3$II$_u$) molecules by argon and nitrogen, and (3) to minimize the formation of N$_2$(C $^3$II$_u$) by the nitrogen atom-atom recombination process and by the energy pooling process from two metastable N$_2$(A $^3$Σ) molecules [9]. The HF (33 MHz) power used for discharge was maintained at a low level, near the discharge cut-off, to minimize the electron density in order to reduce the argon metastable atom relaxation by electron collisions and to avoid the Ar($^3$P$_1$) and Ar($^1$P$_1$) production by electronic collision transfer from Ar($^3$P$_2$) and Ar($^3$P$_0$). The population decays of the Ar($^3$P$_2$) and Ar($^3$P$_0$) were measured by an optical absorption technique. The intensity of the N$_2$(C $^3$II$_u$ $\rightarrow$ B $^3$II$_g$) emission was detected by means of a cooled photomultiplier associated with a photon counting system. Both argon metastable decay and nitrogen second positive emission intensity signals were stored simultaneously in separate multichannel analysers.

![Graphs and plots](image-url)

**Fig. 1.** — Perturbation produced on the Ar($^3$P$_0$) population by laser pumping on the Ar($^3$P$_0$) level with the 7 724 Å laser line, and relative variations of the intensity of N$_2$(C $^3$II$_u$ $\rightarrow$ B $^3$II$_g$) emission; (a) without laser pumping, (b) with laser pumping.
TABLE I

<table>
<thead>
<tr>
<th>$k_0 (^3P_0 \rightarrow v' = 0, K')$</th>
<th>$k_2 (^3P_2 \rightarrow v' = 0, K')$</th>
</tr>
</thead>
<tbody>
<tr>
<td>46</td>
<td>0.5</td>
</tr>
<tr>
<td>47</td>
<td>0.6</td>
</tr>
<tr>
<td>48</td>
<td>0.9</td>
</tr>
<tr>
<td>49</td>
<td>1.1</td>
</tr>
<tr>
<td>50</td>
<td>1.4</td>
</tr>
<tr>
<td>51</td>
<td>2.5</td>
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<td>52</td>
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<td>54</td>
<td>7.5</td>
</tr>
<tr>
<td>55</td>
<td>9.5</td>
</tr>
</tbody>
</table>

For the optical pumping we used a model 375 tunable dye laser pumped by a Krypton-Ion laser model 171 Spectra-Physics. The tunable CW dye laser operated with the Nile Blue dye in multimode with a spectral bandwidth of 0.3 Å and a power output about 100 mW. The laser beam, after being chopped by a rotating disk, was expanded before crossing the discharge cell following its axis. The rotating disk allowed the argon metastable atoms to be pumped by the laser beam in the afterglow during only a small time interval, typically of the order of 1 ms.

3. Results. — The nitrogen second positive emission spectrum, resolved by use of a 1.5 m, SOPRA, Ebert-Fastie scanning monochromator in the afterglow of our experiment, closely resembles that obtained by Stedman and Setser [1].

The typical population decay curves obtained in our experiment are shown in figure 1. For easy comparison we have superposed, for each population scanned, the two curves obtained respectively (a) without laser perturbation and (b) with laser perturbation. The curves were performed with the laser pumping on the Ar($^3P_0$) level, using 7 724 Å dye laser line. Similar results were obtained with the laser pumping on the Ar($^3P_2$) level with the 7 635 Å dye laser line.

Examination of figure 1 leads to some observations: (1) the Ar($^3P_0$) level was depopulated by over 90%, (2) the selective perturbation on the Ar($^3P_0$) level was obtained since the Ar($^3P_2$) population was practically not modified, (3) the transfer efficiency of the perturbation on the N$_2$(C $^3Π_u$, v' = 0) state depends on the vibrational and the rotational quantum numbers v' and K'.

Numerical investigations of the relative perturbations have shown that the low rotational levels of N$_2$(C $^3Π_u$, v' = 0) were populated preferentially by transfer from Ar($^3P_0$) and the vibrational levels v' = 2 and 3 and the high rotational levels of the v' = 0 state were excited by both Ar($^3P_0$) and Ar($^3P_2$) atoms. The measurements of the metastable atom densities and the perturbation rates of N$_2$(C $^3Π_u$ $→$ B $^3Π_g$) emission enabled us to determine the relative values of the coefficient rates for their production by Ar($^3P_0$) and Ar($^3P_2$). Experimental results relative to the high rotational levels of N$_2$(C $^3Π_u$, v' = 0) are given in table I.

For the N$_2$(C $^3Π_u$, v' = 2, 3) levels, checked by N$_2$(C $^3Π_u$ $→$ B $^3Π_g$) (2-0) and (3-0) band head emissions, we have found for $k_0/k_2$ respectively 3 and > 60. The accuracy of these results is about 20 %.

It is interesting to point out from these results that although the vibrational level v' = 2 and the rotational level v' = 0, K' = 48 have approximately the same energies (they are both near the Ar($^3P_2$) energy level) their relative coefficient rates are not the same. The same remark can be made for the v' = 3 level and the (v' = 0, K' = 55) rotational level which lie near the Ar($^3P_0$) energy level. The resonance rule is not applicable in energy transfer between excited atoms and molecules and it seems evident that the high rotational levels of N$_2$(X $^1Σ_g^+$) state contributes to the formation of the high rotational levels of N$_2$(C $^3Π_u$, v' = 0) state by energy transfer from Ar($^3P_2$).

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References