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RELATIVE REACTION RATES IN ROTATIONAL AND VIBRATIONAL EXCITATION OF $N_2(C^3\Pi_u)$ BY $Ar^*(^3P_0)$ AND $Ar^*(^3P_2)$ METASTABLE ATOMS

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Résumé. — Le transfert d'excitation entre $Ar(^3P_0)$, $Ar(^3P_2)$ 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 N_2 . D'autre part, une perturbation sélective est réalisée sur l'un des niveaux $Ar(^3P_0)$, $Ar(^3P_2)$ par la technique de pompage optique utilisant un laser à colorant accordable ; les variations relatives obtenues sur l'intensité des bandes d'émission de N_2 ont permis de déterminer le rapport des coefficients de réaction de transfert d'excitation vibrationnelle et rotationnelle de $N_2(C^3\Pi_u)$ par $Ar(^3P_0)$ et $Ar(^3P_2)$.

Abstract. — The energy transfer reaction between $Ar(^3P_0)$, $Ar(^3P_2)$ and molecules of N_2 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 $N_2(C^3\Pi_u)$ by $Ar(^3P_0)$ and $Ar(^3P_2)$ were obtained.

1. Introduction. — The energy transfer by collisions between excited argon atoms in the $(3p^5 4s)$ 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- N_2 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 $3p^5 4s$ levels, usually designated by 3P_2 , 3P_1 , 3P_0 and 1P_1 , participate in the excitation transfer leading to the formation of the excited state $N_2(C^3\Pi_u)$. 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 $N_2(B^3\Pi_g \rightarrow A^3\Sigma_u^+)$ 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 3P_2 , 3P_1 , 3P_0 and 1P_1 in the formation of the $N_2(C^3\Pi_u, v', K')$ 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 $N_2(C^3\Pi_u, v', K')$ by argon 3P_2 and 3P_0 metastable atoms.

The experiment was performed in the late afterglow where the populations of the 3P_1 and 1P_1 levels were very weak and we have verified that their contribution to the energy transfer can be neglected compared to that of $Ar(^3P_2)$ and $Ar(^3P_0)$. We used the stationary afterglow technique in a HF pulsed electrodeless discharge applied to a Ar : $N_2 = 1\,000 : 1$ 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 $N_2(C^3\Pi_u)$ produced only by transfer from argon metastables. The time dependence study associated with an original perturbation method based on the

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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 $N_2(C^3\Pi_u, v', K')$ 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 $N_2(C^3\Pi_u, v', K')$ molecules before radiative emission, (2) to ensure lower quenching efficiency of both metastable atoms and $N_2(C^3\Pi_u)$ molecules by argon and nitrogen, and (3) to minimize the formation of $N_2(C^3\Pi_u)$ by the nitrogen atom-atom recombination process and

by the energy pooling process from two metastable $N_2(A^3\Sigma)$ 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 $Ar(^3P_1)$ and $Ar(^1P_1)$ production by electronic collision transfer from $Ar(^3P_2)$ and $Ar(^3P_0)$. The population decays of the $Ar(^3P_2)$ and $Ar(^3P_0)$ were measured by an optical absorption technique. The intensity of the $N_2(C^3\Pi_u \rightarrow B^3\Pi_g)$ 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.

FIG. 1. — Perturbation produced on the $Ar(^3P_0)$ population by laser pumping on the $Ar(^3P_0)$ level with the 7 724 Å laser line, and relative variations of the intensity of $N_2(C^3\Pi_u \rightarrow B^3\Pi_g)$ emission; (a) without laser pumping, (b) with laser pumping.

TABLE I

Ratio of the reaction coefficients for the high rotational levels of N₂(C ³Π_u, v' = 0) state excitation by energy transfer from Ar(³P₀) and Ar(³P₂) metastable atoms

K'	46	47	48	49	50	51	52	53	54	55
$\frac{k_0(^3P_0 \rightarrow v' = 0, K')}{k_2(^3P_2 \rightarrow v' = 0, K')}$	0.5	0.6	0.9	1.1	1.4	2.5	2.9	5.2	7.5	9.5

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(³P₀) level, using 7 724 Å dye laser line. Similar results were obtained with the laser pumping on the Ar(³P₂) level with the 7 635 Å dye laser line.

Examination of figure 1 leads to some observations : (1) the Ar(³P₀) level was depopulated by over 90 %, (2) the selective perturbation on the Ar(³P₀) level was obtained since the Ar(³P₂) population was practically not modified, (3) the transfer efficiency of the perturbation on the N₂(C ³Π_u) 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 N₂(C ³Π_u)_{v'=0,1} were populated preferentially by transfer from Ar(³P₂) ; and the vibrational levels v' = 2 and 3 and the high rotational levels of the v' = 0 state were excited by both Ar(³P₂) and Ar(³P₀) atoms. The measurements of the metastable atom densities and the perturbation rates of N₂(C ³Π_u → B ³Π_g) emission enabled us to determine the relative values of the coefficient rates for their production by Ar(³P₀) and Ar(³P₂). Experimental results relative to the high rotational levels of N₂(C ³Π_u)_{v'=0} are given in table I.

For the N₂(C ³Π_u)_{v'=2,3} levels, checked by N₂(C ³Π_u → B ³Π_g) (2-0) and (3-0) band head emissions, we have found for k₀/k₂ 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(³P₂) 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(³P₀) 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 N₂(X ¹Σ_g) state contributes to the formation of the high rotational levels of N₂(C ³Π_u, v' = 0) state by energy transfer from Ar(³P₂).

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