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RELAXATION PROCESSES OF $\text{Xe}^*(^3\text{P}_2)$ METASTABLE ATOMS IN ARGON-XENON MIXTURES

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Résumé. — La décroissance en fonction du temps de la population de l'état métastable $\text{Xe}^*(^3\text{P}_2)$ dans des mélanges Ar-Xe a été mesurée pour des pressions de 0,1 à 40 torr. Ceci a permis la détermination du coefficient de diffusion de $\text{Xe}^*(^3\text{P}_2)$ dans l'argon, soit $81 \pm 4 \text{ cm}^2 \text{ torr s}^{-1}$ à 300 K, et des constantes de destruction de $\text{Xe}^*(^3\text{P}_2)$ par collisions à deux corps contre l'argon k_3 et par collisions à trois corps contre un atome d'argon et un de xénon k_4 :

$$k_3 = (3,5 \pm 0,7) \times 10^{-16} \text{ cm}^3 \text{ at}^{-1} \text{ s}^{-1}$$

$$k_4 = (2,5 \pm 0,5) \times 10^{-32} \text{ cm}^6 \text{ at}^{-2} \text{ s}^{-1}.$$

Abstract. — The decay constant of the concentration of metastable $\text{Xe}^*(^3\text{P}_2)$ in Ar-Xe mixtures has been measured in afterglow at pressures between 0.1 torr and 40 torr. The diffusion coefficient of $\text{Xe}^*(^3\text{P}_2)$ in argon has been found to be $81 \pm 4 \text{ cm}^2 \text{ torr s}^{-1}$ at 300 K. The relaxation rates of $\text{Xe}^*(^3\text{P}_2)$ by two-body collisions with argon k_3 , and by three-body collisions with an argon and a xenon atom k_4 , have been determined to be respectively $(3.5 \pm 0.7) \times 10^{-16} \text{ cm}^3 \text{ at}^{-1} \text{ s}^{-1}$ and $(2.5 \pm 0.5) \times 10^{-32} \text{ cm}^6 \text{ at}^{-2} \text{ s}^{-1}$.

Introduction. — Recently several types of xenon halide excimer laser have been studied and developed. Very often, the mixtures used in such lasers are formed principally of argon with small amounts of xenon and halogen-containing molecules. In these systems, it is expected that the xenon metastable states are the precursors of the excited xenon halide molecules. Therefore, interest in the relaxation processes of xenon metastable states in Ar-Xe mixtures has grown rapidly. From this point of view the results given in the present paper enable, with those of Barbet *et al.* [1] which were obtained in a similar way, a prediction to be made of the relaxation frequency of one xenon metastable state in low pressure mixtures which can be compared with other results obtained recently under different conditions [2], [3], [4].

The relaxation of the $\text{Xe}^*(^3\text{P}_2)$ metastable atoms in a xenon gas has been studied in our laboratory by Barbet *et al.* [1], by monitoring the decay of the concentration of $^3\text{P}_2$ metastable states in a pure xenon

afterglow. In this way, the diffusion coefficient and the reaction rates for two and three-body collisions have been determined.

In the present work we have applied this technique to the study of the relaxation of the $\text{Xe}^*(^3\text{P}_2)$ metastable atoms in Ar-Xe mixtures and from the analysis of the partial pressure dependence of their decay frequency we have determined :

- the diffusion coefficient of the metastable $\text{Xe}^*(^3\text{P}_2)$ in argon,
- the rate constants k_3 and k_4 for destruction of the $\text{Xe}^*(^3\text{P}_2)$ states by the following reactions :

Experimental. — The stationary afterglow technique was used, the mixture of argon and xenon being excited by a pulsed D.C. discharge. The major part of our experimental system has been described previously [1], [5]. In the present study the pyrex discharge cell was cylindrical with dimensions corresponding to

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a fundamental diffusion length $\Lambda = 0.48$ cm. The discharge cell was connected to an ultra high vacuum system which was very carefully baked before use.

The total pressure of the Ar-Xe mixtures was varied between 0.1 and 40 torr and that of Xe between less than 5×10^{-3} and 2 torr. For all the experiments the xenon pressure was small compared to that of argon. Research grade xenon of 99.995 % purity and argon of 99.999 5 % were supplied by the *Air Liquide*.

The discharge was produced by applying a high voltage D.C. pulse of 10 to 20 μ s duration at a repetition frequency of 10 to 1 000 Hz; the discharge current was always lower than 50 mA and generally between 1 and 10 mA.

The decay constant of the $\text{Xe}^*(^3\text{P}_2)$ population was measured by the atomic absorption technique using the 8 819 Å line. The time dependence of the afterglow absorption was determined by means of a multi-channel analyser, built in our laboratory, which had a maximum resolution of 5 μ s [6].

Results. — The evolution of the $\text{Xe}^*(^3\text{P}_2)$ population in an Ar-Xe mixture can be described in the same manner as in pure xenon, which has been described elsewhere [1]. In this way the relaxation frequency can be expressed by :

$$\frac{1}{\tau} = \frac{1}{\Lambda^2 \left(\frac{p_1}{D_0} + \frac{p_2}{D'_0} \right)} + A_1 p_1 + A_2 p_1^2 + A_3 p_2 + A_4 p_1 p_2 \quad (1)$$

where Λ is the diffusion length of the cell ($\Lambda = 0.48$ cm), p_1 and p_2 are respectively the pressures of xenon and argon (torr), D_0 and D'_0 are respectively the diffusion coefficients of $\text{Xe}^*(^3\text{P}_2)$ in xenon and argon at 1 torr and the relaxation frequencies are :

— $A_1 p_1$ for two-body collisions with a xenon atom,

— $A_2 p_1^2$ for three-body collisions with two xenon atoms,

— $A_3 p_2$ for two-body collisions with an argon atom,

— $A_4 p_1 p_2$ for three-body collisions with a xenon and an argon atom,

Strictly speaking a sixth term $A_5 p_2^2$ must be added to take into account the effect of three body collisions with two argon atoms. Some measurements at argon pressure between 20 and 50 torr did not show any increase of the relaxation frequency due to this effect, within the experimental errors. We therefore do not consider it further and we can note that this argument is in good agreement with the value proposed by Kolts and Setser [4] for A_5 .

The electron density of our short duration and relatively low voltage discharge is less than 10^9 electrons/cm³, so that we can neglect, in equation (1), all effects due to the electrons of the afterglow plasma.

The values of D_0 , A_1 and A_2 at 300 K have been determined previously [1] and are respectively taken as :

$$D_0 = 19 \pm 2 \text{ cm}^2 \text{ torr s}^{-1}$$

$$A_1 = 75 \pm 10 \text{ torr}^{-1} \text{ s}^{-1}$$

$$A_2 = 80 \pm 10 \text{ torr}^{-2} \text{ s}^{-1}.$$

The data obtained in the low pressure range, p_2 varying between 0.1 and 4 torr (with $p_1/p_2 < 5 \times 10^{-2}$) are shown in figure 1. The observed increase of τ with p shows that for these pressures, the destruction of metastable atoms is due essentially to collisions against the cell walls, i.e. it is described by the first term (or diffusion term) of equation (1). In order to obtain D'_0 with a good precision we have plotted

FIG. 1. — Decay time of metastable $\text{Xe}^*(^3\text{P}_2)$ atoms versus total pressure of argon-xenon mixtures for xenon partial pressure : $\bullet$ $< 10^{-3}$ torr, $\square$ 3×10^{-3} torr, $\circ$ 5×10^{-3} torr and $\triangle$ 2×10^{-2} torr.

versus $1/p_2$, where $1/\tau$ is the observed relaxation frequency. $1/\tau'$ increases linearly with $1/p_2$ and the slope of the line is D'_0/Λ^2 , the value obtained for D'_0 is $81 \pm 4 \text{ cm}^2 \text{ torr s}^{-1}$ at 300 K. To calculate $1/\tau'$ it is necessary to know A_3 and A_4 ; this is not a difficulty because a rough estimated value of D'_0 allows approximate values of A_3 and A_4 to be obtained which are sufficient for the calculation of the corrective terms in $1/\tau'$.

In the high pressure range, p_2 varying between 4 and 40 torr, the destruction of metastable states by two or three-body collisions with argon and xenon atoms becomes dominant. To extract A_3 and A_4 from the

FIG. 2. — Relaxation of metastable Xe*(³P₂) atoms in the high pressure range : $1/\tau'' p_2$ versus p_1 ; p_1 and p_2 are respectively the xenon and argon partial pressures and $1/\tau''$ is the corrected relaxation frequency (see text). Typical error bars are shown.

high pressure data, we have plotted in figure 2. $1/\tau'' p_2$ versus p_1 ; where

$$\frac{1}{\tau''} = A_3 p_2 + A_4 p_1 p_2 = \frac{1}{\tau} - \frac{1}{A^2 \left(\frac{p_1}{D_0} + \frac{p_2}{D'_0} \right)} - A_1 p_1 - A_2 p_1^2$$

i.e. $1/\tau''$ is the observed relaxation frequency corrected for diffusion and collisions with xenon atoms only. The slope of the line in figure 2 gives A_4 and the intercept A_3 . The values obtained at 300 K are

$$A_3 = 11 \pm 2 \text{ torr}^{-1} \text{ s}^{-1}$$

and $A_4 = 26 \pm 5 \text{ torr}^{-2} \text{ s}^{-1}$.

They are given in term of reaction rates in table I.

For all the results presented here it should be noted that the greater part of the estimated experimental error is due to a rather imprecise knowledge of the xenon partial pressure.

Discussion. — Our results are given in table I, where are also given values reported by other workers.

We can see that our value for the diffusion coefficient D'_0 agrees very well with that of Kolts and Setser [4], who worked in the same pressure range as us but using a flowing afterglow technique. Palkina *et al.* [7] have proposed a method to calculate the diffusion coefficient of metastable rare gases in the same gas, it seems that, considering only the long range dipole-dipole interaction of metastable atom with ground state rare gas atom, an extension of their work to the case under study leads to a clear discrepancy between theoretical and experimental values, the theoretical value being lower by a factor of two.

As regards reaction rates, the results of Kolts and Setser [4] were obtained in experimental conditions as described above. The experimental conditions in which Rice and Johnson [2] and Gleason *et al.* [3] worked were very different. They observed the time dependence of the emission of molecular Xe₂ and Ar₂ in dense mixtures (¹) of argon and xenon excited by a pulsed energetic electron beam. If we consider the different ways used to measure these reaction rates we can conclude that they are in satisfactory agreement.

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TABLE I

Diffusion coefficient and rate constants of the destruction of Xe*(³P₂) in Ar-Xe mixtures

Process	Coefficient	This work	Other works
Diffusion in argon	D'_0	$(2.6 \pm 0.15) \times 10^{18} \text{ at cm}^{-1} \text{ s}^{-1}$	$(2.5 \pm 0.2) \times 10^{18} \text{ at cm}^{-1} \text{ s}^{-1}$ [4]
Xe*(³ P ₂) + Ar → products	k_3	$(3.5 \pm 0.7) \times 10^{-16} \text{ cm}^3 \text{ at}^{-1} \text{ s}^{-1}$	$\begin{cases} (4 \pm 0.7) \times 10^{-16} \text{ cm}^3 \text{ at}^{-1} \text{ s}^{-1} & [3] \\ (5 \pm 0.7) \times 10^{-16} \text{ cm}^3 \text{ at}^{-1} \text{ s}^{-1} & [4] \end{cases}$
Xe*(³ P ₂) + Ar + Xe → products	k_4	$(2.5 \pm 0.5) \times 10^{-32} \text{ cm}^6 \text{ at}^{-2} \text{ s}^{-1}$	$\begin{cases} (2.15 \pm 0.25) \times 10^{-32} \text{ cm}^6 \text{ at}^{-2} \text{ s}^{-1} & [3] \\ 2.3 \times 10^{-32} \text{ cm}^6 \text{ at}^{-2} \text{ s}^{-1} & [2] \end{cases}$

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(¹) Rice and Johnson [2] argon pressure between 10³ and 19 × 10³ torr, xenon pressure between 500 and 10³ torr.
Gleason *et al.* [3] argon pressure between 1.5 × 10³ and 9 × 10³ torr, xenon pressure between 2 × 10⁻³ and 8 torr.