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RELAXATION PROCESSES OF Xe*(3P₂) METASTABLE ATOMS IN ARGON-XENON MIXTURES

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Résumé. — La décroissance en fonction du temps de la population de l'état métastable Xe*(3P₂) 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 Xe*(3P₂) dans l'argon, soit 81 ± 4 cm² torr s⁻¹ à 300 K, et des constantes de destruction de Xe*(3P₂) par collisions à deux corps contre l'argon k₃ et par collisions à trois corps contre un atome d'argon et un de xénon k₄ :

\[ k₃ = (3.5 \pm 0.7) \times 10^{-16} \text{ cm}^3 \text{ at}^{-1} \text{ s}^{-1} \]
\[ k₄ = (2.5 \pm 0.5) \times 10^{-32} \text{ cm}^6 \text{ at}^{-2} \text{ s}^{-1} \]

Abstract. — The decay constant of the concentration of metastable Xe*(3P₂) in Ar-Xe mixtures has been measured in afterglow at pressures between 0.1 torr and 40 torr. The diffusion coefficient of Xe*(3P₂) in argon has been found to be 81 ± 4 cm² torr s⁻¹ at 300 K. The relaxation rates of Xe*(3P₂) by two-body collisions with argon k₃, and by three-body collisions with an argon and a xenon atom k₄, have been determined to be respectively (3.5 ± 0.7) \times 10^{-16} cm³ at⁻¹ s⁻¹ and (2.5 ± 0.5) \times 10^{-32} cm⁶ at⁻² 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 Xe*(3P₂) 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 ³P₂ 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 Xe*(3P₂) 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 Xe*(3P₂) in argon,
— the rate constants k₃ and k₄ for destruction of the Xe*(3P₂) states by the following reactions :

\[
\text{Xe}^*_{(3P₂)} + \text{Ar} \xrightleftharpoons[k₃]{k₄} \text{Xe}^*_{(3P₁)} + \text{Ar} \rightarrow \text{Xe}^* + \text{Ar} + hν
\]

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
a fundamental diffusion length $A = 0.48$ 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 $5 \times 10^{-3}$ 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 99.9995% were supplied by the Air Liquide.

The discharge was produced by applying a high
voltage D.C. pulse of 10 to 20 $\mu$s duration at a repetition
frequency of 10 to 1000 Hz; the discharge current
was always lower than 50 mA and generally
between 1 and 10 mA.

The decay constant of the Xe*(3P$_2$) 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 $\mu$s [6].

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

$$\frac{1}{\tau} = \frac{1}{A^2 \left( \frac{p_1}{D_0} + \frac{p_2}{D_0^*} \right)} + \frac{A_1 p_1 + A_2 p_1^2 + A_3 p_2 + A_4 p_1 p_2}{D_0} \tag{1}$$

where $A$ is the diffusion length of the cell ($A = 0.48$ 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 Xe*(3P$_2$) 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 col-
lisions 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 pro-

The electron density of our short duration and
relatively low voltage discharge is less than $10^9$
electrons/cm$^3$, so that we can neglect, in equation (1),
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 $p_1/p_2 \lesssim 5 \times 10^{-2}$) are shown in figure 1. The observed increase of $\tau$ 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

$$\frac{1}{\tau} = \frac{D_0^*}{p_2 A^2} = \frac{1}{A_1 p_1 - A_2 p_1^2 - A_3 p_2 - A_4 p_1 p_2 - \frac{p_1 A^2}{D_0}}$$

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 $D_0^*/A^2$, 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. 1. — Decay time of metastable Xe*(3P$_2$) atoms versus total
pressure of argon-xenon mixtures for xenon partial pressure :

- $< 10^{-3}$ torr, $\square 3 \times 10^{-3}$ torr, $\bigcirc 5 \times 10^{-3}$ torr and
$\Delta 2 \times 10^{-2}$ torr.
FIG. 2. — Relaxation of metastable Xe*(3P₂) atoms in the high pressure range : \(1/\tau \) versus \( p_2 \); \( p_1 \) 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.

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 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

<table>
<thead>
<tr>
<th>Process</th>
<th>Coefficient</th>
<th>This work</th>
<th>Other works</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion in argon</td>
<td>( D_0 )</td>
<td>( (2.6 \pm 0.15) \times 10^{18} ) at ( \text{cm}^{-1} \text{s}^{-1} )</td>
<td>( (2.5 \pm 0.2) \times 10^{18} ) at ( \text{cm}^{-1} \text{s}^{-1} ) [4]</td>
</tr>
<tr>
<td>Xe*(3P₂) + Ar ( \rightarrow ) products</td>
<td>( k_3 )</td>
<td>( (3.5 \pm 0.7) \times 10^{-16} ) cm³ at ( \text{cm}^{-1} \text{s}^{-1} )</td>
<td>( (4 \pm 0.7) \times 10^{-16} ) cm³ at ( \text{cm}^{-1} \text{s}^{-1} ) [3]</td>
</tr>
<tr>
<td>Xe*(3P₂) + Ar + Xe ( \rightarrow ) products</td>
<td>( k_4 )</td>
<td>( (2.5 \pm 0.5) \times 10^{-32} ) cm⁶ at ( \text{cm}^{-2} \text{s}^{-1} )</td>
<td>( (2.15 \pm 0.25) \times 10^{-32} ) cm⁶ at ( \text{cm}^{-2} \text{s}^{-1} ) [3]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( 2.3 \times 10^{-32} ) cm⁶ at ( \text{cm}^{-2} \text{s}^{-1} ) [2]</td>
<td></td>
</tr>
</tbody>
</table>

References


\footnote{1)} Rice and Johnson [2] argon pressure between \( 10^3 \) and \( 19 \times 10^3 \) torr, xenon pressure between 500 and \( 10^3 \) torr. Gleason et al. [3] argon pressure between \( 1.5 \times 10^3 \) and \( 9 \times 10^3 \) torr, xenon pressure between 2 \( \times 10^{-3} \) and 8 torr.