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KINETICS OF THE ENERGY TRANSFERS IN ArXe MIXTURES

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Résumé.— Dans les mélanges Ar-Xe, l'étude spectroscopique des émissions dans l'ultra-violet lointain a montré des transferts d'énergie d'excitation importants de l'argon vers le xénon. Les émissions continues de l'argon diminuent rapidement au profit des émissions moléculaires et atomiques du xénon lorsque de faibles quantités de xénon sont ajoutées à Ar. Le spectre des mélanges contenant quelques pour cent de Xe est comparable à celui du xénon pur. L'analyse cinétique du continuum de l'argon à 127 nm montre que les transferts d'énergie se produisent non seulement depuis l'état moléculaire $\text{Ar}_2^*(^3\Sigma_u^+)$, responsable du 2ème continuum de l'argon ($k_2 = 1,5 \cdot 10^7 \text{ torr}^{-1} \text{ s}^{-1}$) mais aussi depuis le précurseur atomique de Ar_2 ($k_2 = 2,5 \cdot 10^7 \text{ torr}^{-1} \text{ s}^{-1}$). Les sections efficaces de ces deux processus sont très grandes.

Abstract.— In ArXe mixtures, spectroscopic studies of the far UV emissions have shown the presence of large excitation energy transfers from argon to xenon. The argon continuums decrease rapidly giving way to molecular and atomic Xe emissions as small quantities of Xe are added to the Ar. The spectra of mixtures containing just a few percent Xe are similar to spectra of pure xenon. Kinetic analysis of the argon continuum at 127 nm shows that energy transfers occur not only from the $\text{Ar}_2^*(^3\Sigma_u^+)$ molecular states which give rise to the second argon continuum ($k_1 = 1.5 \cdot 10^7 \text{ torr}^{-1} \text{ s}^{-1}$) but also from the atomic precursors of Ar_2 ($k_2 = 2.5 \cdot 10^7 \text{ torr}^{-1} \text{ s}^{-1}$). The cross sections of both processes are very high.

INTRODUCTION. The emission of light in rare gas mixtures has been widely studied over the last years in the field of halogen and excimer laser applications (1).

The emissions of pure rare gases in the far UV, at pressures of a few hundred torr, correspond to transitions from a weakly bound molecular state (1 or $^3\Sigma_u^+$) to the dissociative ground state ($^1\Sigma_g^+$) (2).

In mixtures of two rare gases the action of the heavier gas is seen to be very important since the characteristic emissions of the latter appear with high intensities even when it is present only in traces. The transfer processes therefore have extremely high cross sections (3). The present report concerns ArXe mixtures.

EXPERIMENTAL SET-UP. A representation of the apparatus is given in figure 1. The emission spectra are obtained by counting the anode pulses of a P.M. (called U) set to detect single photons. Excitation is pro-

duced by an ^{241}Am α -source. The shape of the light pulses is determined with a time-amplitude conversion method : the PM. U records an isolated photon at instant t_1 and a second PM determines an arbitrary but constant zero time t_0 . The intervals $t_1 - t_0$ are measured by time amplitude conversion and recorded on a multichannel analyser. The histogram of the time delays ($t_1 - t_0$) represents the time variation of the density of the excited species which emits the studied transition. The pulses are numerically analysed and the time constants governing them calculated by a least squares method.

EMISSION SPECTRA OF ArXe MIXTURES. The emission spectra were recorded from 110 to 300 nm at total pressures of between 100 and 600 torr and xenon concentrations varying from a few ppm to 10 %. An example is given in figure 2 where the influence of xenon is shown in argon samples at 600 torr.

Figure 1 : Experimental set-up. Position 1 is used to obtain a trace of the emission spectra, the multichannel analyser is working in the multiscale range. Position 2 corresponds to the determination of the light pulse shapes.

Even for extremely low xenon concentrations (~ 10 ppm), the argon spectrum is modified. The characteristic argon continuum at 127 nm decreases giving way to two Xe resonance lines : $^1P_1 \rightarrow ^1S_0$ at $\lambda = 129.6$ nm and $^3P_1 \rightarrow ^1S_0$ at 147 nm. This process continues as the level of Xe increases and finally only the emissions of Xe are present. At a total pressure of 600 torr and Xe concentration as low as 0.1 %, the spectrum is qualitatively the same as that of pure xenon ; at 173 nm there is an emission which is attributed to the second Xe continuum. At low pressures (100 torr) an identical process occurs but at higher concentrations.

The spectroscopic study shows the high efficiency of the transfer phenomena from one gas to another and also the importance of the molecular excitation processes of the minority gas.

Figure 2 : Spectra of the Ar-Xe mixtures at varying xenon concentrations. The total pressure is constant, $p_T = 600$ torr (--- 10 ppm, 100 ppm, — 1 000 ppm of Xe).

Figure 3 shows the great difference between the spectrum of the mixture containing 1 % xenon and that obtained at the same to-

tal pressure of pure argon (600 torr), it is also very different to that obtained at the same partial pressure of pure xenon (6 torr).

Excitation transfer can either occur from molecular (Ar_2^*) states or from atomic precursor states or even via both paths at the same time.

To clarify this situation a kinetic study was carried out on the wavelength corresponding to the maximum of the argon continuum.

Figure 3 : The three spectra in this figure demonstrate the efficiency of the transfer processes. Addition of just 1 % Xe to Ar at 600 torr gives completely different emission spectra ; the argon continuum gives way to those of Xe and yet, xenon alone at the same partial pressure does not present these continuous emissions.

KINETIC STUDY AT $\lambda = 127$ nm. This study was carried out at constant gas pressure. In pure argon, the shape of the light pulse is described by the algebraic sum of three exponential terms :

$$I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}$$

τ_1 represents the lifetime of the molecular state Ar_2^* , $\tau_1 = 2.86 \mu\text{s}$, τ_2 and τ_3 concern the primary states $^3\text{P}_1$ and $^3\text{P}_2$ respectively.

$$1/\tau_2 = 1.6 p_{\text{Ar}}^2 + 490 p_{\text{Ar}} + 6 \cdot 10^4$$

$$1/\tau_3 = 13.8 p_{\text{Ar}}^2 + 580 p_{\text{Ar}}$$

where τ_1 and τ_3 are in seconds and p_{Ar} is in torr.

The presence of xenon can be seen through a change in the constants τ_1 and τ_2 and also the appearance of an additional term : $A_4 e^{-t/\tau_4}$; at constant argon pressures (400 and 700 torr), the new time constants are such that :

$$\tau_1'^{-1} = \tau_1^{-1} + k_1 p_{\text{Xe}}$$

$$\tau_2'^{-1} = \tau_2^{-1} + k_2 p_{\text{Xe}} \quad (\text{figures 4 and 5})$$

$$\tau_4^{-1} = k_4 p_{\text{Xe}} + k_3$$

k_4 , k_1 and k_2 are independent of p_{Ar} and have the values :

$$k_1 = 1.5 \cdot 10^7 \text{ torr}^{-1} \text{ s}^{-1}$$

$$k_2 = 2.5 \cdot 10^7 \text{ torr}^{-1} \text{ s}^{-1}$$

$$k_4 = 3.2 \cdot 10^5 \text{ torr}^{-1} \text{ s}^{-1}$$

Figure 4 : Linear variation of the reciprocals of the time constants τ_4 and τ_2' against the Ar pressure ($p_{\text{Xe}} = 0.105 \text{ torr}$).

The previous result was confirmed by operating at constant p_{Xe} (0.105 and 0.014 torr). These measurements also allowed the

expression of k_3 to be found :

$$k_3 = 280 p_{Ar} + 2 \cdot 10^5 \quad (k_3 \text{ in } s^{-1} \text{ and } p_{Ar} \text{ in torr}) \quad (\text{figure 6}).$$

Figure 5 : Linear variation of the reciprocals of the time constants τ_4 , τ'_1 and τ'_2 against the pressure of Xe ($p_{Ar} = 700$ torr).

Figure 6 : Variation of the reciprocals of the time constants τ_4 and τ'_2 against the Ar pressure ($p_{Xe} = 0.105$ torr).

DISCUSSION. Referring to the kinetic schema of pure Ar (fig. 7), it can be seen that xenon interacts with the atomic and the molecular levels of Ar. Constant k_1 represents the decay of the molecular state $Ar_2^*(^3\Sigma_u^+)$ through 2-body collision.

This process explains the decrease of the argon continuums as the Xe concentration rises. The value of k_1 was determined by Lechner (5) and Chen (6) as being $6.3 \cdot 10^6$ and $7.9 \cdot 10^6$ respectively -these are appreciably lower than those of Gleason (4) $k_1 = 1.4 \cdot 10^7 \text{ torr}^{-1} s^{-1}$ and Oka (11) $k_1 = 1.64 \cdot 10^7 \text{ torr}^{-1} s^{-1}$ which are in good agreement with our experimental determination.

The cross section of the process deduced from our value of k_1 ($\sigma = 1.1 \cdot 10^{-14} \text{ cm}^2$) is also close to that given by Gedanken ($\sigma = 3 \cdot 10^{-13} \text{ cm}^2$). As this author mentions, molecule-atom collisional energy transfers are very efficient for resonant states in which the energy coincides with that of the emission of the donor gas. It can be seen that in reaction (1), the resonating 1P_1 xenon state fills this condition as is shown by the fact that the resonating transition : $Xe(^1P_1) \rightarrow Xe(^1S_0) + h\nu$ at 129 nm is observed under our experimental conditions.

Furthermore the term $k_2 p_{Xe}$ in $\tau_2'^{-1}$ shows

that a 2-body collision reaction occurs on the 3P_1 state of argon :

Considering the value of k_2 , the energy transfer is very efficient since the 3P_1 state is partly responsible for the creation of the radiative molecular state Ar_2^* , reaction (2) also contributes to the disappearance of the molecular emission. Gleason did not observe this phenomenon because his working pressure was too high. Chen's value (6) ($k_2 = 7.2 \cdot 10^6 \text{ torr}^{-1} \text{ s}^{-1}$) is, as previously, lower than ours.

Gedanken (3) reports that for atom-atom collisions the energy transfers become more efficient as the energies of the excited levels approach. The 5f states of xenon are therefore probably populated through the 3P_1 state of Ar since the energy coincides, a cascade could then lead to population of the 5d levels. This hypothesis is confirmed by the fact that laser transitions from the 5d Xe states were reported by Lawton (7) and by Davies (8) in ArXe mixtures.

The metastable 3P_2 state of argon however does not seem to be affected by the presence of Xe, this signifies that a reaction of the type :

is negligible with respect to 2- and 3-body collisions with argon :

This result is in agreement with the value of the constant k given by Piper (10) ($k = 5.9 \cdot 10^6 \text{ torr}^{-1} \text{ s}^{-1}$). In effect, when working at $p_{\text{Ar}} = 700 \text{ torr}$ and $p_{\text{Xe}} = 0.7 \text{ torr}$ the frequency of reaction (3) is $4 \cdot 10^6 \text{ s}^{-1}$ i.e. low with respect to processes (4) and (5) ($7 \cdot 10^6 \text{ s}^{-1}$).

The additional exponential term of time constant τ_4 can be related to the presence of the Xe resonance line originating from the 1P_1 state which is added to the argon continuum. The lifetime we calculated for this state ($k_4^{-1} \sim 5 \mu\text{s}$) is close to that of Sadeghi (9) ($7 \mu\text{s}$) however his decay constant by collision with Xe ($k_4 = 2.1 \cdot 10^6 \text{ torr}^{-1} \text{ s}^{-1}$) is higher.

In order to obtain more accurate information on the development of the 1P_1 state it would be necessary to work at pressures for which the argon continuum does not appear.

Figure 7 : Kinetic scheme of the energy transfer processes in Ar-Xe mixtures. Transfers from the molecular Ar_2^* and the atomic state $\text{Ar}(^3P_1)$ are in competition.

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