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COLLISIONAL DEPOPULATION OF A HIGH-LYING P STATE OF POTASSIUM

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Résumé. — On a mesuré les sections efficaces de dépopulation collisionnelle totale du niveau 10 P du Potassium, à 470 K, induite par collision avec des atomes de Potassium ou de gaz rare : $Q(K) = 6\,000 \pm 3\,000 \text{ Å}^2$; $Q(\text{He}) = 18 \pm 6 \text{ Å}^2$; $Q(\text{Ar}) = 8 \pm 3 \text{ Å}^2$; $Q(\text{Xe}) = 40 \pm 15 \text{ Å}^2$. L'importance des transferts d'excitation électronique vers les niveaux voisins est indiquée. Il est montré que l'électron de valence a un comportement *quasi-libre*.

Abstract. — Total cross-sections for the collisional depopulation of the 10 P level of Potassium by Potassium and rare gases have been measured, with the following results : $Q(K) = 6\,000 \pm 3\,000 \text{ Å}^2$; $Q(\text{He}) = 18 \pm 6 \text{ Å}^2$; $Q(\text{Ar}) = 8 \pm 3 \text{ Å}^2$; and $Q(\text{Xe}) = 40 \pm 15 \text{ Å}^2$. The importance of the electronic excitation transfer to neighbouring levels is clearly demonstrated as well as the influence of the quasi-free behaviour of the valence electron.

Because the outer electron is in a very large, weakly bound orbit, atoms in high-lying or Rydberg states exhibit rather unique properties : long radiative lifetimes, giant polarizabilities and great sensitivity to various perturbations (electric field, collision processes...). Investigations of some of these properties have already begun [1, 2].

Experiments on excitation transfer and total collisional depopulation (quenching) of lower excited states of alkali atoms have been performed in our laboratory [3]. At the same time, the theoretical calculation of alkali-rare gas potential curves [4] permits a satisfactory approach to the problem of inelastic collisions at thermal energies. The extension of such experimental and theoretical studies to Rydberg states seems to be very interesting. We report here, for the first time, an experimental study of the collisional depopulation of the 10 P level of Potassium due to collisions with Potassium or rare gas atoms in their respective ground states.

We have measured the total quenching cross-sections and have also determined the cross-section for a particular quenching process : the electron excitation transfer to a neighbouring, well-defined, atomic level. We are concerned with two reactions : one involving the total quenching

where $K(10\text{ P})$ is a Potassium atom lying in the 10 P level, X either a ground-state Potassium (K) or rare gas (G) atom, Q_x the quenching cross-section, and

$K(\neq 10\text{ P})$ a Potassium atom in its final (ionic or neutral) state, and the second reaction involving the particular specific deactivation

where $K(f)$ is a Potassium atom lying in the final f atomic level, $Q_x(10\text{ P} \rightarrow f)$ the cross-section associated with the considered process and ΔE the energy splitting between the two levels. The K and G subscripts will indicate that the corresponding quantities refer to (Potassium-Potassium) and (Potassium-Rare gas) collisions respectively. Figure 1 shows the levels involved.

The experimental set-up shown in figure 2 is quite similar to the one described in ref. [3]. A reference cell, filled with Potassium and kept at a fixed temperature, allows us to monitor both the wavelength and the intensity of the light source, which consists of a flash-lamp pumped dye laser (Rhodamine 6 G), associated with an extra-cavity frequency doubling device that uses a non-linear crystal (ADA) [5]. The UV pulses ($\lambda = 2\,992 \text{ Å}$) have a half-width time duration of about $3.7 \mu\text{s}$, an output power of 0.5 mJ per pulse and a linewidth of 0.4 Å . The repetition rate is one pulse per 6 s. The power is enough to ensure a high population of the 10 P level in spite of the very low oscillator strength, which is a typical feature of the Rydberg states. To our knowledge it is the first time that the population of a highly excited P state of an alkali atom is directly achieved by selective optical excitation.

FIG. 1. — Energy levels of the Potassium atom involved in this experiment.

FIG. 2. — Schematic diagram of the apparatus : P : monochromator and high-speed photon counting system ; T : trigger.

We observed the population of the 10 P level by looking at the direct fluorescence of the (10 P → 3 D) transition ($\lambda = 8\,418\text{ Å}$). At Potassium densities of about 10^{13} cm^{-3} , numerous other optical transitions, coming from upper levels (9 D, 11 S, 9 F, 11 P, 10 D, 12 S, 12 P) collisionally populated from the 10 P are found to be present. We did not study the lower levels because of the cascading effects that occur (except for the 8 F level). The variation of the population of the 9 D, 11 S, 9 F and 11 P levels, due to the addition of rare gas densities of about 10^{15} cm^{-3} , has also been observed. All the experiments are performed at a temperature of 470 K.

The determination of the Q_K and Q_G quenching

cross-section is achieved by looking at the variation in the intensity ratio of the fluorescence line ($\lambda = 8\,418\text{ Å}$) from each of the two cells, as a function of Potassium or rare gas density in the experimental cell (in the later case the Potassium density is kept at a fixed value). We modify the classical Stern-Volmer method to our experimental conditions. The requirements for its validity [6] (low stimulated emission, no absorption or collisional broadening, low repopulation of the 10 P level, ...) are fulfilled in a satisfactory way. The results we obtain are shown in table I. For the derivation of the cross-section we use the radiative lifetime of the 10 P level as computed from the results of Anderson and Zilitis [7], since their computation also produce good agreement with the Sodium lifetime results [1].

TABLE I

Comparison between the 10 P quenching cross-sections and the total elastic scattering cross-sections for electrons of 0.15 eV energy

Process	$Q\text{ (Å}^2\text{)}$	Process	$Q_e\text{ (Å}^2\text{)}$
K-K	$6\,000 \pm 3\,000$	e^- -K	$\approx 1\,000$
K-He	18 ± 6	e^- -He	≈ 6
K-Ar	8 ± 3	e^- -Ar	≈ 1.5
K-Xe	40 ± 15	e^- -Xe	≈ 11

We have also determined the excitation transfer cross-section from the 10 P level to the group of levels (9 D, 11 S), when the collision partner is a ground-state Potassium atom. The experimental method (sensitized fluorescence) and the derivation of the cross-section are quite similar to those described in ref. [3]. The obtained value is

$$Q_K(10\text{ P} \rightarrow (9\text{ D}, 11\text{ S})) = (800 \pm 400)\text{ Å}^2.$$

In the following discussion we will refer to neutral and ionic channels for reactions whose final product is, respectively, an atom lying in a well-defined excited state or an ion. The value of Q_K ($6 \times 10^{-13}\text{ cm}^2$) is very high (the geometrical cross-section value is about $9 \times 10^{-13}\text{ cm}^2$). Two types of mechanisms (neutral or ionic channel) can achieve the collisional depopulation of the 10 P level. We can observe numerous neutral channels and we measure one of them to be about 10 % of the quenching. When considering the statistical weights and the respective position in the energy diagram of the energetically accessible levels, one can see that the neutral channels account for an important part of the 10 P level quenching.

Lee and Mahan [8] have shown that the two following reactions (ionic channels) are present (see Fig. 3) :

but the values of the corresponding cross-section are not known. A recent paper [9] indicates that the associative ionization cross-section for the 7 D level of Cesium is about $3 \times 10^{-15} \text{ cm}^2$. In the case of Helium the cross-sections are of the same order of magnitude. Even if the cross-sections for reactions (1) and (2) would reach 10^{-14} cm^2 , the quenching of the 10 P would still remain mainly due to inelastic collisions giving rise to neutral channels. Thus, since the ionic channels do not contribute more than a few percent to the total 10 P depopulation value, collisional ionization does not represent the main quenching process for this level.

FIG. 3. — Estimated potential energy curves for K_2 and K^+ .

We will now discuss the values obtained for Q_G . When considering the data concerning the potential curves of the (K^+ -rare gas) ions [10], the ionic channels seem to be energetically forbidden, since the 10 P level lies about 1600 cm^{-1} below the ionization limit. Thus only neutral channels can contribute to the quenching. Some of these have been observed. The Q_G cross-sections (see Table I) are noticeably higher than the values reported in the case of lower excited levels of alkali atoms [11], for which the number of energetically accessible channels are less numerous. The Potassium-rare gas energy curves correlated to the levels under study have already been obtained using the method described in ref. [4]. We hope that a comparison between experimental and theoretical excitation transfer cross-sections, calculated from the potential energy curves, will be possible in the near future.

The outer electron of an alkali atom lying in a Rydberg state is very weakly bound (the average value of the orbital radius is about 55 Å in our case).

Thus it seems very interesting to compare the values of Q_K and Q_G to the values of the elastic scattering cross-sections of electrons on the corresponding targets at an incident energy of the electron equal to those of the valence electron in the 10 P level ($\approx 0.15 \text{ eV}$). These cross-sections [12] are also reported in table I. Two main features appear. First, the quenching cross-sections are always higher than the corresponding elastic scattering cross-sections Q_E ; second, the quenching cross-sections behave quite similarly to the corresponding Q_E , in that there is a great difference between the Potassium-Potassium and Potassium-rare gas cross-section values and a similar variation as a function of the considered rare-gas. One cannot attribute the low values of Q_G to the absence of ionic channels, since they only make a small contribution to the high Q_K value. Instead, these low values seem related to the quasi-free behaviour of the valence electron, and its weak interaction with the noble gases in our experimental conditions. Studies concerning the collisional broadening and shifts of the Rydberg states of the alkali atoms [13] have clearly pointed out the importance of the quasi-free behaviour of the outer electron. The comparison mentioned here suggests future experimental as well as theoretical investigations. The determination of the quenching cross-sections as a function of the principal quantum number n (i.e. the energy of the valence electron) would permit one to check the reliability of the comparison with the elastic scattering of slow electrons. In particular the behaviour of Q_G would noticeably differ according to whether the elastic scattering by the considered gases exhibit or do not exhibit the Ramsauer-Townsend effect. The proposed analogy however would not give rise to quenching cross-sections directly related to the geometrical cross-sections (i.e. $\sim n^4$), since the elastic scattering cross-sections of very low energy electrons exhibit various behaviours, according to the nature of the targets. A theoretical approach, taking into account the quasi-free behaviour of the valence electron pointed out in this study, seems to be possible. Although previous theoretical treatments have called this fact to mind, the experimental results reported here clearly point out the necessity of including this behaviour.

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