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Electronic energy transfer between state selected metastable argon atoms and ground state krypton atoms

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Résumé. — La réaction de transfert d'énergie des atomes métastables Ar (3P2) et Ar (3P0) à l'atome Kr a été étudiée dans la post-décharge d'un mélange Ar-Kr. La constante de décroissance de la densité des atomes métastables a été mesurée pour obtenir les coefficients de relaxation des atomes Ar (3Pj) par Kr. Dans des expériences séparées, le niveau Ar (3P2) a été dépeuplé dans la phase de post-décharge à l'aide d'un laser accordable continu. La comparaison des intensités d'émission à partir des niveaux excités de Kr avec et sans dépeuplement laser a été utilisée pour obtenir les coefficients de réaction pour l'excitation des niveaux de Kr par Ar (3P2) et Ar (3P0). L'excitation de Kr par des atomes Ar (3P2) est ~ 40 fois plus efficace que par des atomes Ar (3P0).

Abstract. — The excitation transfer reactions from Ar (3P2) and Ar (3P0) to Kr were studied in the afterglow of a pulsed discharge. The time decay of the metastable concentrations was monitored to obtain total quenching rate constants for removal of Ar (3Pj) by Kr. In separate experiments, Ar (3P2) was optically depopulated in the afterglow by use of a tunable cw dye laser. Comparison of emission intensities from excited Kr levels with and without laser perturbation was used to assign relative rate constants for excitation of Kr levels by Ar (3P2) and Ar (3P0). The Kr excitation by Ar (3P2) was found to be ~ 40 times more efficient than by Ar (3P0).

1. Introduction.

In recent years, studies of the quenching reactions of the heavier metastable Rg (3P2) and Rg (3P0) states have grown rapidly due not only to fundamental interest in these processes but also because the excited rare gas atoms are often the active species in laser systems [1, 2]. Most of the experimental data pertain to the 3P2 state; total quenching rate constants [3-5] and product channel branching fractions [6-8] have been determined for a wide variety of reagents. Although some quenching rate constants have also been measured for Ar (3P0) [3a], relatively little other attention has been directed to the higher energy 3P0 state, which for Ar (and Ne) can account for ~ 10 % of the total metastable density in discharge excited systems. Complete characterization of the product channels from Rg (3P0) is usually hampered by interference from the predominant 3P2 species.

Only recently have these states been separated and significant differences found in their relative quenching mechanisms. Sadeghi et al. [9] examined the Ar (3P2,0) + N2 excitation transfer reaction and found that the relative populations of the N2 (C, 3Πj) product vibrational and rotational substates were dependent on the Ar (3Pj) precursor. Golde and Poletti observed different atomic halogen and molecular argon halide electronic state distributions from Ar (3P2) and Ar (3P0) reacting with several halogen containing molecules [10]. Finally, the Penning ionization reactions of Ne (3P0) with Ar, Kr, and Xe shows a marked propensity for formation of the Rg+ (3P1/2) ion state relative to Rg+ (3P3/2); for Ne (3P2), the Rg+ (3P1/2) is only slightly favoured [11].

In this paper we present a study of the excitation transfer from Ar (3P2,0) atoms to ground state Kr atoms, which also shows large differences between the two metastable Ar states. Piper et al. [12] have previously examined this reaction using the flowing afterglow technique and report that the only observable Kr levels excited from Ar (3Pj) were Kr (2P8) and Kr (2P7) (see Fig. 1), in the ratio of ~ 9/1. Weak emission from
Kr (2P₂) and an ArKr excimer also were observed but were attributed to formation from Ar (³P₀) [12]. However, since the sum of the formation rate constants for these products was less than the Ar (³P₀) quenching rate constant, other Kr states, presumably Kr (2P₆) and Kr (2P₇), accounted for the main products from quenching of Ar (³P₀) [12].

The present work utilizes the stationary afterglow technique to measure total quenching rate constants, and coupled with laser depopulation of Ar (³P₂) in the afterglow, to characterize the products from Ar (³P₀) + Kr. Rate constants for excitation of specific Kr levels by Ar (³P₀) relative to Ar (³P₂) were determined by monitoring Kr emission intensities and Ar (³P₂,0) concentrations, with and without the laser perturbation. Absolute rate constants for Ar (³P₀) excitation are obtained from the known values of the corresponding Ar (³P₂) rate constants. These experiments indicate: i) two-body quenching of Ar (³P₂) by Kr is ~ 40 times faster than for Ar (³P₀), ii) both Ar metastable states give Kr (2P₆) and Kr (2P₇) as the major (> 95 %) products, but with Kr (2P₆) favoured from Ar (³P₀) and Kr (2P₇) favoured from Ar (³P₀), and iii) quenching of Ar (³P₀) also proceeds by a fast three-body reaction involving Ar and Kr.

2. Experiment.

The experimental apparatus and techniques have largely been described in detail in previous publications from this laboratory [9, 13]. Research grade Ar and Kr (99.999 5 %) were separately flowed through a cylindrical (D = 4 cm, L = 25 cm) Pyrex cell. A dc pulsed discharge was applied to the cell at a frequency 20-200 Hz to create metastable Ar atoms. Both the discharge pulse duration (~ 100 µs) and current (~ 5 mA) were adjusted to maximize the metastable densities in the afterglow. The Kr product channel rate constants were measured at low (~ 0.2 torr Ar) pressure in order to minimize secondary collisions of Kr* with the Ar buffer [14]; the mole fraction of Kr in these experiments was < 0.5 %. Measurements of the quenching rate constants were performed at Ar pressures ranging from 1-7 torr. An MKS Baratron capacitance manometer (model 221 A) was used for all pressure measurements.

Both Ar (³P₀) absorption signals, giving the metastable concentrations, and the near IR Kr* emission signals from the cell were detected with a 0.6 meter Jobin-Yvon monochromator equipped with a Hamamatsu R 928 photomultiplier tube and by using photon counting and data accumulation techniques. In some experiments the Kr resonance line at 123.6 nm was also monitored using a 1 meter VUV monochromator and channeltron (R.T.C.) detector. The VUV monochromator was interfaced to one base of the cell via a LiF window. In determining the Kr formation rate constants, absorption and emission measurements were made only during a 1-2 ms detection gate located ~ 1 ms after the cessation of the discharge. For determining the quenching rate constants, the entire metastable decay curves were accumulated in a multichannel analyser and passed on to a computer for later analysis. A radiofrequency powered Ar lamp provided 763.5 nm and 794.8 nm line sources for absorption by Ar (³P₂) and Ar (³P₀), respectively. Metastable concentrations were obtained from the absorption rate measurements using conversion factors given previously [15]. For typical operating conditions without laser pumping, the concentration of Ar (³P₂) was ~ 10¹⁰ cm⁻³ with [Ar (³P₀)]/[Ar (³P₂)] about 0.15.

Laser depopulation of Ar (³P₂) in the afterglow was achieved by use of a tunable cw dye laser (Spectraphysics, Model 375) pumped by a Kr⁺ ion laser (Model 171). Oxazine 725 dye was used to produce the 696.5 nm line of Ar (2P₂ ← ³P₂). This line was chosen from several possibilities because favourable branching fractions from Ar (2P₂) [16] permit simultaneous depopulation of Ar (³P₂) and enhancement of the Ar (³P₀) concentration. The dye laser output linewidth, 0.03 nm, was reduced to 0.003 nm by means of an auxiliary intracavity etalon. Fine tuning of the laser wavelength was optimized by observation of the optogalvanic signal from a separate Ar discharge cell. The laser beam was brought to the reaction cell through an optical fibre and expanded by means of a spherical lens before entering the cell along its axis. The typical laser output power used was 250 mW and, under these conditions, Ar (³P₂) was depopulated by more than 99 %.
3. Results.

3.1 Metastable Quenching Rate Constants. — Following discharge excitation in the presence of Kr, the metastable Ar ($^3P_{2,0}$) atoms can decay by diffusion and several collisional processes involving Ar, or Kr or both together. At a fixed Ar pressure, the Kr induced decay frequency, $k_{Q(2)}$, of either metastable state can be described by

$$1/\tau - K = k_{Q(2)}[\text{Kr}],$$

where $k_{Q(2)}$ is the effective two-body quenching rate constant by Kr atoms at the given Ar pressure, $\tau$ is the measured decay time of the observed metastable species in the presence of Kr and $K$ represents the decay frequency of the same metastable in the absence of Kr (due to diffusion and collisional deactivation by ground state Ar atoms alone). Figure 2 shows the decay of Ar ($^3P_{2}$) and Ar ($^3P_{0}$) at 1.03 torr Ar and with a Kr density of $5.4 \times 10^{14}$ atoms cm$^{-3}$. Both these curves and others that were obtained could be represented by a single decay constant and, as can be seen, the decay of Ar ($^3P_{0}$) is appreciably slower than for Ar ($^3P_{2}$). Figure 3 shows the variation of the decay constants (l.h.s. cf. Eq. 1), obtained from curves similar to those shown in figure 2, with the Kr concentration. The slopes of the plots give directly the quenching rate constants which were extracted from the data by a least squares analysis. Several experiments performed at 1.00 ± 0.03 torr gave average values of $4.90 \pm 0.20 \times 10^{-12}$ cm$^3$ molec$^{-1}$ s$^{-1}$ and $2.43 \pm 0.25 \times 10^{-13}$ cm$^3$ molec$^{-1}$ s$^{-1}$ for $k_{Q(2)}$ and $k_{Q(0)}$, respectively, where the error limits represent one standard deviation from the mean. We estimate the absolute uncertainty in the $k_{Q}$, which stems from uncertainties in the measured Kr concentration and decay time measurements, to be less than 15 %. The error in the relative values should be less than this as decay curves for the two metastables were always obtained back to back with identical Kr concentrations.

The $k_{Q}$ measured at 1 torr represent the effective two-body rate constants since a three body component may also be contributing,

$$\text{Ar}^* + \text{Kr} \rightarrow \text{products} \quad (2)$$

$$\text{Ar}^* + \text{Ar} + \text{Kr} \rightarrow \text{products} \quad (3)$$

In the flowing afterglow experiments, Piper et al. [12] observed emission from an ArKr excimer which they attributed to formation from three-body quenching of Ar ($^3P_{0}$). Thus reaction 3 could be an important quenching pathway even at relatively low Ar pressures. Measurements of $k_{Q(2)}$ were performed at several Ar pressures ranging from 1 to 7 torr. For Ar ($^3P_{2}$), no significant variation of $k_{Q(2)}$ was found over the limited pressure range that could be studied, indicating that $k_{Q(2)}(2)$ is too small to be detected. However, for Ar ($^3P_{0}$), $k_{Q(0)}(0)$ was found to increase with increasing Ar pressure as shown in figure 4. The plot is linear and from the intercept and slope values of $1.14 \pm 0.10 \times 10^{-13}$ cm$^3$ molec$^{-1}$ s$^{-1}$ and $4.35 \pm 0.40 \times 10^{-10}$ cm$^6$ molec$^{-2}$ s$^{-1}$ were deduced for $k_{Q(2)}(0)$ and $k_{Q(0)}(0)$, respectively. Attempts were made to extend the plot to higher pressures but these efforts were unsuccessful because of the rapid decay of Ar ($^3P_{2,0}$) at pressures higher than 10 torr.

The measured rate constants are summarized in table I and can be compared to results obtained by other laboratories. For Ar ($^3P_{2}$), most of the determination support a value of $5 \times 10^{-12}$ cm$^3$ molec$^{-1}$ s$^{-1}$
for \( k_Q(2) \). The two exceptions are due to Bourene and LeCalvé [4a] and Bochkova [17] where \( k_Q(2) \) is 2-3 times larger. Bourene and LeCalvé used high energy electron excitation of an Ar/Kr mixture along with \( N_2 \) as a tracer of Ar \((3p_0)\) [4a]. Possible ambiguities in the precursor of the tracer emission could account for their larger result. The discrepancy with Bochkova is more difficult to rationalize since she used the same experimental techniques as in this work. However, no details of her measurements were given and the result was quoted only as an estimate. Based on the good agreement with all the other determinations, we conclude that our measurement is reliable.

Two previously reported \( k_Q(0) \), both obtained at \( \sim 1 \) torr in a flowing afterglow apparatus, differ by an order of magnitude. Velazco et al. [3a] used absorption to follow Ar \((3p_2)\) and found

\[
k_Q(0) = 2.3 \times 10^{-12} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}
\]

while Golde and Poletti [19] derived

\[
k_Q(0) = 3.4 \times 10^{-13} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}
\]

from monitoring the decay of tracer emission as a function of added Kr. In the latter case only \( k_Q(2)/k_Q(0) (=18) \) could be accurately determined and \( k_Q(0) \) was assigned from assuming

\[
k_Q(2) = 6 \times 10^{-12} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}.
\]

Our results are in agreement with Golde and Poletti since at one torr Ar pressure we obtain

\[
k_Q(2)/k_Q(0) \approx 20
\]

and thus confirm the much lower value for \( k_Q(0) \). However, we emphasize the fact that \( k_Q(0) \) contains both a two- and three-body deactivation of Ar \((3p_0)\).

### 3.2 Krypton excitation rate constants.

A portion of the Kr fluorescent spectrum excited in the afterglow is shown in figure 5a without laser perturbation. Our observations of the spectrum generally resemble those of Piper et al. [12] in that only the Kr \((2p_6)\) and Kr \((2p_7)\) levels are strongly populated. In fact, the only other emissions observed aside from that shown in figure 5a were the Kr lines at 819.0 nm, 829.8 nm, and 123.6 nm with the first two also originating from Kr \((2p_{6,7})\) and the latter being a consequence of radiative cascade [12]. Although both Ar \((3p_2)\) and Ar \((3p_0)\) are present, the Kr emission is due almost entirely \((\geq 99 \%)\) to excitation by Ar \((3p_2)\) because of its much larger concentration \([\text{Ar}(3p_2)/\text{Ar}(3p_0) \sim 6]\) and the fact that quenching of Ar \((3p_0)\) by Kr is much slower than for Ar \((3p_2)\).

Taking into account the intensity of the observed lines at 760.2 and 769.5 nm along with the branching fractions for these transitions [20], we find the relative formation rate of Kr \((2p_6)\) to Kr \((2p_7)\) to be 8.5/1 in excellent agreement with the value of 8.6/1 obtained by Piper et al. [12]. If we consider that quenching of Ar \((3p_2)\) by Kr results only in excitation of Kr \((2p_{6,7})\), our measured \( k_Q(2) \) can be partitioned into formation rate constants of \(4.39 \times 10^{-12} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}\) and \(0.51 \times 10^{-12} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}\) for Kr \((2p_6)\) and Kr \((2p_7)\), respectively. These values are given in table I and agree with those obtained by Piper et al. [12] and Bochkova [17].

When Ar \((3p_2)\) is depopulated by 696.5 nm laser radiation, the absolute intensities of the Kr \((2p_{6,7})\) emission lines are reduced and their relative magnitude changes as shown in figure 5b. In addition, emission from Kr \((2p_4)\) at 758.7 nm, previously obscured by the strong 760.2 nm line, is observed. Since atomic absorption gave no measurable signal from Ar \((3p_2)\), the spectrum in figure 5b is due primarily to excitation.
Table I. — Rate constants for Ar ($3P_2$) + Kr and Ar ($3P_0$) + Kr reactions.

<table>
<thead>
<tr>
<th>Process</th>
<th>This work</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar ($3P_2$) + Kr $→$ products</td>
<td>$4.90 \pm 0.20$</td>
<td>$6.0 (\text{f}), 14.0 (\text{f}), \sim 9.7 (\text{f}), \sim 4.8 (\text{f}), \sim 4 (\text{f})$</td>
</tr>
<tr>
<td>$→$ Ar + Kr* ($2P_2$)</td>
<td>$4.39 \pm 0.20$</td>
<td>$5.5 (\text{f}), 4.9 (\text{f})$</td>
</tr>
<tr>
<td>$→$ Ar + Kr* ($2P_7$)</td>
<td>$0.51 \pm 0.10$</td>
<td>$0.6 (\text{f}), 0.6 (\text{f})$</td>
</tr>
<tr>
<td>Ar ($3P_0$) + Kr $→$ products</td>
<td>$0.114 \pm 0.01 (0.243) (\text{f})$</td>
<td>$(2.3) (\text{f}), (0.34) (\text{f})$</td>
</tr>
<tr>
<td>$→$ Ar + Kr* ($2P_2$)</td>
<td>$0.003 \pm 0.001$</td>
<td>$0.0034 (\text{f})$</td>
</tr>
<tr>
<td>$→$ Ar + Kr* ($2P_7$)</td>
<td>$&lt; 0.035$</td>
<td></td>
</tr>
<tr>
<td>$→$ Ar + Kr* ($2P_7$)</td>
<td>$0.078 \pm 0.008$</td>
<td></td>
</tr>
<tr>
<td>Ar ($3P_0$) + Kr + Ar $→$ products</td>
<td>$4.35 (\text{f}) \pm 0.40$</td>
<td>$&lt; 0.5 (\text{f})$</td>
</tr>
<tr>
<td>$→$ Ar + Kr* + Ar</td>
<td>$2.5 (\text{f})$</td>
<td></td>
</tr>
</tbody>
</table>

(*) Unless otherwise noted rate constants are in units of $10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.

(\text{f}) Ref. 3a.

(\text{f}) Ref. 4a.

(\text{f}) Ref. 17.

(\text{f}) Ref. 18.

(\text{f}) Ref. 19.

(\text{f}) Ref. 12.

(\text{f}) Effective 2-body rate constant at 1 torr for comparison with other measurements.

(\text{f}) The three-body rate constants have units of $10^{-15} \text{ cm}^3 \text{ molec}^{-2} \text{ s}^{-1}$.

from Ar ($3P_0$). Rate constants for excitation of Kr ($2P_6$) and Kr ($2P_7$) by Ar ($3P_0$) were assigned relative to excitation from [Ar ($3P_2$)] by a comparison technique. The desired ratio, $k_0/k_2$, is obtained from:

$$R = \frac{k_0}{k_2} = \frac{I^{[3P_2]} - I^{[3P_2]}_{[3P_0]}}{I^{[3P_0]} - I^{[3P_0]}_{[3P_2]}}$$

(4)

where $I$ is the intensity of the Kr line diagnostic of either Kr ($2P_6$) (760.2 nm) or Kr ($2P_7$) (769.5 nm), $I^{[3P_2]}$ is the concentration of Ar ($3P_2$), and the superscripts refer to quantities with (w) and without (wo) laser perturbation. The average of several runs gave $R = 0.15 \pm 0.02$ for Kr ($2P_7$) and $R = 0.008 \pm 0.004$ for Kr ($2P_6$) which combined with the Ar ($3P_2$) rate constants yield $7.8 \times 3.5 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ for $k_0 (2P_7)$ and $k_0 (2P_6)$, respectively.

Both $R (2P_6)$ and $R (2P_7)$ were derived from equation 4 with $I^{[3P_2]}_{[3P_0]}$ set equal to zero as no absorption from Ar ($3P_0$) was found during laser pumping. However, small absorption signals of less than 0.5% would not have been observed with our detection system and some residual Ar ($3P_2$) could still have contributed to the Kr excitation. Since $R (2P_7)$ is relatively large compared to $R (2P_6)$, excitation of Kr ($2P_7$) from Ar ($3P_0$) is negligible compared to Ar ($3P_0$) and $k_0 (2P_6)$ should be reliable. On the other hand, for Kr ($2P_6$), the contribution from residual Ar ($3P_2$) could be significant because of the more than two order of magnitude difference in $k_0 (2P_6)$ and $k_2 (2P_6)$. In fact by taking into account the atomic absorption detection limit, it is impossible to rule out Ar ($3P_2$) as the sole precursor of Kr ($2P_6$) even during laser pumping. Thus $R (2P_6)$ obtained from equation 4 with $[\text{Ar} (3P_2)]^{[3P_2]} = 0$ must be regarded as an upper limit and $k_0 (2P_6) \leq 3.5 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.

The values for $k_0 (2P_6)$ and $k_0 (2P_7)$ are given in table 1 along with $k_0 (2P_2) = 3.0 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. Formation of Kr ($2P_2$) from Ar ($3P_2$) is endothermic and equation 4 cannot be used to determine $k_0 (2P_2)$. Instead $k_0 (2P_2)$ was assigned from $k_0 (2P_6)$ by comparison of the 758.7 nm and 769.5 nm atomic line intensities during laser pumping along with the appropriate branching ratios [20]. Assuming that $k_0 (2P_6)$ is approximately correct, the sum of the Kr excitation rate constants agrees within experimental error with our value of $k_0 (0)$, suggesting that all major products from two-body quenching of Ar ($3P_0$) have been identified. The only other possible products could be Kr ($2P_{8-10}$) and the Kr ($4s$) levels. No emission from Kr ($2P_{8-10}$) was observed in our experiments and formation of these levels must be negligible. Direct production of the Kr ($4s$) levels is more difficult to rule out. However, during experiments the intensity of the Kr resonance line at 123.6 nm was also monitored. The decrease in intensity of this line with laser pumping was always comparable (within 10%) to that calculated on the basis of the corresponding decrease of the infrared lines weighted by their branching ratio for the emission to Kr ($3P_1$) [20]. Thus we conclude that direct produc-
4. Discussion.

The total two-body quenching rate of Ar\(^{(3P_0)}\) by Kr is approximately 40 times slower than for Ar\(^{(3P_2)}\). Both Ar metastable states give Kr\(^{(2P_6)}\) and Kr\(^{(2P_7)}\) as the major exit channels. However, for Ar\(^{(3P_2)}\), Kr\(^{(2P_6)}\) is favoured by ~9/1 while for Ar\(^{(3P_0)}\), Kr\(^{(2P_7)}\) is populated at least 2 times more efficiently than Kr\(^{(2P_6)}\). An additional exit channel from Ar\(^{(3P_0)}\) is Kr\(^{(2P_5)}\); but, this product accounts for less than 5% of the total two-body quenching of Ar\(^{(3P_0)}\).

Most of these results can be qualitatively explained by the schematic potential curves shown in figure 6 and a simple curve-crossing model. For quenching of Ar\(^{(3P_2)}\), no symmetry restrictions exist for the products since the entrance channel has curves with molecular configurations of \(0^-\), \(1\) and \(2\) while the Kr\(^{(2P_6)}\) and Kr\(^{(2P_7)}\) exit channels are \(0^-\), \(1\) and \(0^-\), \(1\), respectively. Piper et al. [12] have used the Landau-Zener theory to explain the larger formation rate constants from Ar\(^{(3P_2)}\) should be much smaller, which is consistent with our experimental results. In addition, Kr\(^{(2P_2)}\) is statistically favoured since both the \(0^-\) and \(1\) components can interact with the entrance channel while for Kr\(^{(2P_6)}\), interaction occurs only with \(0^-\) and \(1\) components. If all components are similar in shape and cross the entrance channel potential at roughly the same internuclear distance, the predicted \(k_{e}(2P_7)/k_{e}(2P_6)\) ratio is 1.5, which can be compared with experimental ratio of ~2.1. The relatively good agreement is somewhat fortuitous since the repulsive part of the Kr\(^{(2P_6,7)}\)-Ar potentials is not well known and the different components can be expected to have different repulsive characters and coupling strengths with the entrance channel potential. Nevertheless, the product channel branching fractions from quenching of Ar\(^{(3P_0)}\) are qualitatively consistent with the simple curve-crossing mechanism, although a more quantitative comparison will have to await more accurate Ar-Kr potentials.

Quenching of Ar\(^{(3P_0)}\) was also found to proceed by a 3-body step involving Ar and Kr and we obtained a relatively large rate constant of \(4.4 \times 10^{-30}\) cm\(^6\) molec\(^{-2}\) s\(^{-1}\), two orders of magnitude larger than the most of the known 3-body reaction coefficient of rare gas metastable atoms. In their study, Piper et al. [12] observed an ArKr continuum emission peaking at 756.5 nm which they attributed to formation from Ar\(^{(3P_0)}\). From the pressure dependence of the band intensity, they derived a 3-body collision rate constant of \(2.5 \times 10^{-30}\) cm\(^6\) molec\(^{-2}\) s\(^{-1}\), in reasonable agreement with our measured 3-body quenching rate coefficient of Ar\(^{(3P_0)}\). However, there is no evidence of the ArKr formation in the spectrum shown in figure 5b or those taken at Ar pressures as high as 2 torr. From the detection limit of our system, we can derive an upper limit to the ArKr formation rate constant of \(5 \times 10^{-31}\) cm\(^6\) molec\(^{-2}\) s\(^{-1}\) which is considerably smaller than the quenching rate constant. Thus the products from three-body quenching of Ar\(^{(3P_0)}\) remain unidentified. It is possible that the

![Fig. 6. — Schematic potential energy curves for Ar-Kr (redrawn from Ref. 12). The numbers give the \(\Omega\) components. Abscissa is interatomic distance.](image-url)

internuclear distance and with a better matching of the slopes than the Kr\(^{(2P_5)}\)-Ar curves. Thus, both factors favor Kr\(^{(2P_2)}\) as the preferred exit channel, as is experimentally observed. Using approximate numerical potentials, Piper et al. [12] obtained good agreement between predicted and observed \(k_{2}(2P_6)/k_{2}(2P_7)\) ratio.

The Ar\(^{(3P_0)}\)-Kr entrance channel contains only a single \(0^-\) curve while the Kr\(^{(2P_6)}\) exit channel is \(0^+\). Thus mixing of these two curves cannot take place and only a minor amount of Kr\(^{(2P_6)}\) is observed experimentally. On the other hand, formation of both Kr\(^{(2P_6)}\) and Kr\(^{(2P_7)}\) can be expected since these states have at least one curve which crosses the Ar\(^{(3P_0)}\)-Kr potential and is of the proper symmetry \(0^-\) or \(1\). However, the intersections will be too abrupt to allow for efficient transfer. Thus, compared to Ar\(^{(3P_2)}\) the Kr excitation rate constants from Ar\(^{(3P_0)}\) should be much smaller, which is consistent with our experimental results. In addition, Kr\(^{(2P_7)}\) is statistically favoured since both the \(0^-\) and \(1\) components can interact with the entrance channel while for Kr\(^{(2P_6)}\), interaction occurs only with \(0^-\) and \(1\) component. If all components are similar in shape and cross the entrance channel potential at roughly the same internuclear distance, the predicted \(k_{e}(2P_7)/k_{e}(2P_6)\) ratio is 1.5, which can be compared with experimental ratio of ~2.1. The relatively good agreement is somewhat fortuitous since the repulsive part of the Kr\(^{(2P_6,7)}\)-Ar potentials is not well known and the different components can be expected to have different repulsive characters and coupling strengths with the entrance channel potential. Nevertheless, the product channel branching fractions from quenching of Ar\(^{(3P_0)}\) are qualitatively consistent with the simple curve-crossing mechanism, although a more quantitative comparison will have to await more accurate Ar-Kr potentials.
three-body collision destroys the symmetry restrictions of the two-body Ar (3P_0) + Kr collision and results in formation of excited Kr levels. Since the Kr* fluorescent spectra were obtained at low pressure (0.2 torr), the three-body contribution to the measured excitation rate constants would be negligible.

References

[15] Sadeghi, N., Doctorat d'Etat, Université de Grenoble (1974), unpublished. Metastable densities were calculated by using \( l \times [3P_2] = 3.2 \times 10^{12} \, A \) and \( l \times [3P_0] = 1.67 \times 10^{11} \, A \), where \( l \) is optical passe length, \( A \) is the absorption rate, and \([3P_{2,0}]\) atom densities.