REACTIONS OF Ar^+ ($^2P_{1/2}$) AND Ar^+ ($^2P_{3/2}$) IN ARGON

M. Grössl, H. Helm, T.D. Märk and M. Langenwalter
Inst.f. Experimentalphysik, Abt.f. Kernphysik u.Gaselektronik
Leopold Franzens Universität, A 6020 Innsbruck, Austria

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ABSTRACT

In their parent gas atomic rare gas ions $R^+(^2P_{3/2})$ are converted in three body collisions into stable bound molecular ions R_2^+(I 1/2 u). The upper atomic ion state $R^+(^2P_{1/2})$ is regarded to be lost in a three body collison as well. However the molecular state directly accessible to this ion, R_2^+ (II 1/2 u), is weakly bound and may either decay or be collisional dissociated. In the present study the rate of singly charged atomic ions of Ar and Kr have been measured in a stationary afterglow experiment and evidence for reactions of both atomic states has been found.

1. INTRODUCTION

The transport phenomena and reaction mechanism of rare gas ions in their parent gases have been studied with different techniques by a large number of investigators. The quantitative knowledge of transport data has been improved enormously by means of precision drift tube experiments so that theories including fine structure phenomena may be tested.

Nevertheless, the understanding of the reaction mechanisms is still poor. For instance in argon values given in the literature for the effective 3-body reaction rate coefficient for the conversion of the singly charged atomic ion into the dimer ion

(1) $Ar^+ + 2\ Ar \rightarrow Ar_2^+ + Ar$
scatter between $0.6 \cdot 10^{-31}$ and $4.7 \cdot 10^{-31} cm^6 s^{-1}$. Hyatt and Knewstubb 1972 and Liu and Conway 1975 attributed an observed anomaly in the reaction behaviour of the atomic argon ions to the presence of ions in the two fine structure states, the ground state $Ar^+(^2P_{3/2})$ and the metastable state $Ar^+(^2P_{1/2})$. A definite difference in reactivity of the two fine structure states of Ne^+ and Kr^+ in their parent gases could be observed experimentally in swarm experiments by Helm and Elford 1978. As a common evidence all mentioned investigators observed a much lower destruction efficiency due to reactions for the metastable ionic state than for the ground state ion. In addition, a strong dependence of the metastable ion population on the neutral impurity concentration has been observed. However only one quantitative experimental results about the reactivity of the $^2P_{1/2}$ ion state is reported so far. Liu and Conway 1975 report an upper limit, because they cannot totally exclude side reactions with impurities for the destruction frequency of $Ar^+(^2P_{1/2})$ in Ar.

2. EXPERIMENTAL METHOD AND RESULTS

The ions were produced in a pulsed hollow cathode glow discharge (Fig.1) and monitored with a mass spectrometer as a function of time as described elsewhere (Langenwalter et al. 1977). Careful attention was payed to minimize the impurity level in the gases used. Measurements have been made at neutral gas pressures between 0.3 and 3 Torr at 297 K.

In Ar two different exponential decays of the Ar^+-signal could be observed at reduced gas pressures higher than 1.6 Torr, as is shown in Fig.2 for instance. From the measurements at low gas pressures (<1.5 Torr), where only one exponential decay has been observed, a value for the zero field mobility of 1.55 cm^2/Vs could be deduced in very good agreement with drift tube data. Using this value effective 3-body rate coefficients for all pressures are calculated and plotted versus gas pressure (Fig.3) in a semi-logarithmic diagram. The full dots, which are related either to the single exponential decay mode or at high pressures to the fast decay during the early afterglow, lie between ± 10% of a mean value of the rate coefficient of $2{,}4 \cdot 10^{-31}\,cm^6 s^{-1}$. Evidently this loss rate corresponds to the conversion process (1) of the $^2P_{3/2}$ ground state ions. The open circles, corresponding to the slow decay at high pressures, show a very strong pressure dependence. This slow decay period in the late afterglow may be dominated by reactions of $Ar^+(^2P_{1/2})$ ions for which Helm and Varney 1978 proposed a reaction model. For their model the effective 3-body rate coefficients versus pressure are shown by the full line. The dotted line represents results reported by Liu and Conway (see above). The pressure behavior observed in the present experiment (open circles) suggests an additional production process for the Ar^+-ions in the very late afterglow at high pressures.

From the energy balance one would expect a similar behavior for Kr^+ in Kr. However we could not observe double exponential decay curves for Kr^+. Nevertheless the analysis of the measured single exponential decay suggests strongly for pressures higher than 2 Torr the existence of a second, superimposed slow decay. The observed Kr^+ ion decay signal can be analysed in the usual way (single exponential decay mode) yielding a reduced mobility value of 0,9 cm^2/Vs. A 3 body rate coefficient of $2{,}5 \cdot 10^{-31}\,cm^6 s^{-1}$ for the conversion of the ground state Kr^+ ion into the molecular ion (analogous to process (1))has been obtained.

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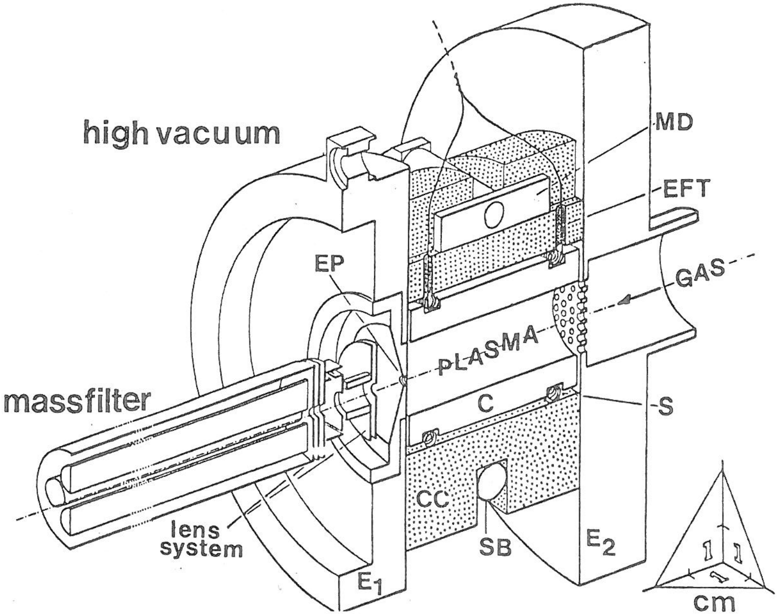

Fig.1 Hollow cathode stationary afterglow apparatus - a schematic diagram of the discharge vessel and the ion-sampling device. C - cylindrical hollow cathode, E1 - Anodeplate serving as extraction probe with the extractionhole EP, E2 - Anodeplate, CC - ceramic cylinder, MD - mechanical driving setup to move the hollow cathode in front of the extraction hole perpendicular to the cylinder axis, S - metallic springs, SB - slide bar, EFT - electrical feedthrough.

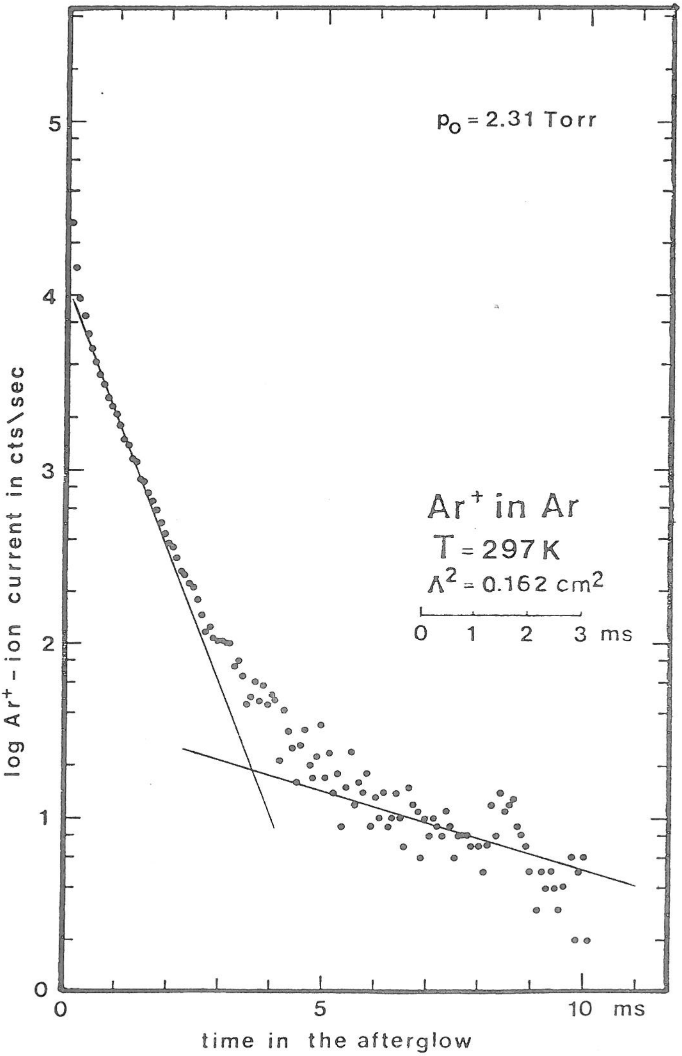

Fig.2 Measured time dependent Ar^+ ion current at high pressures: The double exponential decay curve

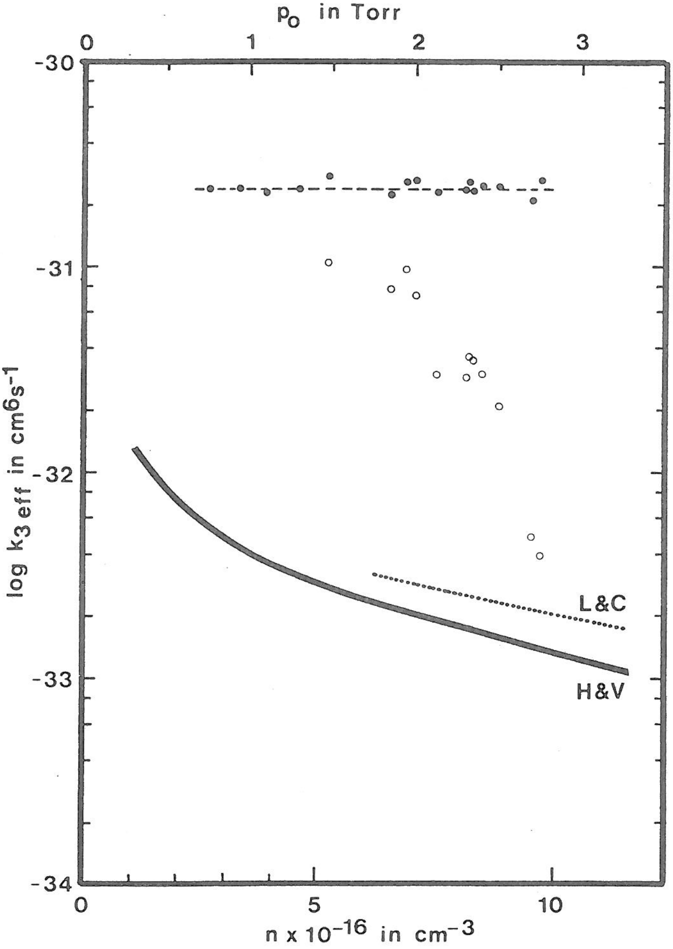

Fig.3 Effective 3-body rate coefficient as a funtion of gas density (or pressure) calculated from the first(●) and the second(o) decay period of the measured decay curves. Predictions for the $^2P_{1/2}$ion: ···· Liu a. Conway, ▬ Helm a. Varney