International Journal of Mass Spectrometry 280 (2009) 119–127

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

State-specific reactions and autoionization dynamics of Ar^{2+} produced by synchrotron radiation

Pietro Franceschi[a], Roland Thissen[b,*], Odile Dutuit[b], Christian Alcaraz[c], Heloise Soldi-Lose[c], Davide Bassi[a], Daniela Ascenzi[a], Paolo Tosi[a], Jan Zabka[d], Zdenek Herman[d], Marcello Coreno[e], Monica de Simone[f]

[a] *Dipartimento di Fisica, Università di Trento, Via Sommarive 14, Povo, Trento, Italy*
[b] *Laboratoire de Planétologie de Grenoble, CNRS UMR 5109, UJF Bâtiment D de physique, 120 rue de la piscine, 38041 Grenoble, France*
[c] *Laboratoire de Chimie Physique, CNRS UMR 8000, Université Paris-Sud, Orsay, France*
[d] *V. Čermàk Laboratory, J. Heyrovsky Institute of Physical Chemistry, Acad. Sci. of the Czech Republic, Dolejškova 3, 182 23 Praha 8, Czech Republic*
[e] *CNR – IMIP, Rome Branch c/o Gasphase Beamline@Elettra, Trieste, Italy*
[f] *CNR – Laboratorio Nazionale TASC, INFM, Trieste, Italy*

ARTICLE INFO

Article history:
Received 2 June 2008
Received in revised form 11 July 2008
Accepted 18 July 2008
Available online 30 July 2008

Keywords:
Argon
Dication
Photoionization
Ion molecule reaction
Autoionization

ABSTRACT

The long-lived excited states of doubly charged rare gases can markedly affect their reactivity. In this paper we demonstrate the presence of strong state-specific effects in the charge exchange of Ar^{2+} (^3P, ^1D and ^1S) with several neutral targets (He, Ne, Kr, Xe, D_2, and CH_4). State sensitive measurements have been performed by producing the different Ar^{2+} electronic states via tunable synchrotron radiation (Elettra-Trieste, Italy and SuperACO-Orsay, France). From the product ion yield data of charge transfer, state-selected total cross-sections have been deduced. Using the state-specific reactivity of Ar^{2+} towards different neutral targets, it has been possible to extract the photon-energy-dependent production branching of the three doubly charged states and to investigate the autoionization dynamics of neutral or singly charged Ar in the vicinity of the double ionization threshold.

1. Introduction

The reactions of doubly charged ions are important in many ionized media including plasmas, ionospheres and astrophysical environments, where charged species are produced by high energy electrons and photons. In the case of rare gas atoms, ionization can produce excited states whose radiative quenching to the ground state is forbidden. Such long-lived species hold a large amount of internal energy which may influence their reactivity.

One-photon double ionization is forbidden in the frozen orbital-independent particle model; however it widely occurs due to electron correlations. For Ar dication, three different ionic states (^3P, ^1D and ^1S) can be populated in the 43–52 eV energy range. The threshold of the ^3P ground state occurs at 43.39 eV, the onset of the ^1D lies at 45.13 eV, while, at even higher energies, the ^1S opens up at 47.51 eV [1].

The branching ratios of the three states have been reported in a two electron coincidence measurement [2] performed at 48.4 eV photon energy. It led to the conclusion that the three dicationic states are populated according to their statistical weights. This near statistical population of dication final states was quite unexpected for two reasons: (i) according to the Wannier law, the partial cross-section for double ionization rises approximately linearly from threshold amplifying the final states of lowest energy and (ii) extended Wannier theory [3] states that, for symmetry reasons, the ^3P final state is the most favored one in direct double ionization near threshold. Spectra of Eland et al. [2] contain intense features associated to autoionization of singly charged ions and are responsible for the near statistical population of the final states. Eland et al. comes to the conclusion that "our understanding of the processes of double photoionization and of autoionization branching is still unsatisfactory". In the present work, we profit from target-dependent state-specific reactivity and photon energy-dependent measurements to deduce the branching ratio of the three states from double ionization threshold up to 52 eV.

Charge transfer, quenching and association reactions of doubly charged rare gas ions were thoroughly investigated in drift tube-mass spectrometer (SWARM) experiments by Johnsen and Biondi

* Corresponding author.
E-mail address: Roland.Thissen@obs.ujf-grenoble.fr (R. Thissen).

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doi:10.1016/j.ijms.2008.07.020

[4,5]. State-selected rate constants for the reactions of Ar^{2+} (and all the other rare gas dications) with rare gases were measured. State selection was obtained by profiting from the different mobilities of various ionic states in the buffer gas [6]. In addition, to obtain "pure" ionic beams, the authors took advantage of the quenching of selected Ar^{2+} states when Ar or He were used as buffer gases. Under these conditions, the rate constant for ^1D reactivity was given only as a rough estimate, since the mobility signal of this state overlapped with the ^3P signal and since collisional quenching could have contributed to the loss of ^1D ions. In the same paper, experimental results were rationalized by the relative positions of the diabatic potential energy curves for the $X^{2+} + Y$ and $X^+ + Y^+$ systems. Reactions with exothermicities of ~4 eV turn out to be fast, in good agreement with the "reaction window" model based on the Landau Zener formalism [7,8] and the small reaction rate constant for excited state reactants is as expected with this energy-defect criterion.

Almost at the same time, another series of investigations was performed by means of drift experiments [9–12]. Neutral targets range from rare gas atoms (helium, argon and xenon) to molecules (H_2, N_2, O_2, CO_2, CH_4, C_2H_2, and NO_2). It is worth noting that, in these experiments, state-selection over the dication electronic states was obtained by using chemical reactions with a buffer gas in order to selectively remove some Ar^{2+} states from the mixture produced in the ion source, as indicated by Johnsen and Biondi [4].

At low temperatures (30 K), rate constants for some Ar^{2+} (^3P) reactions were investigated in CRESU experiments [13].

In the case of the Ar^{2+} + He reaction, state-selected information was obtained in a crossed beam experiment, where it was possible to distinguish the relative contributions of the Ar^{2+}(^3P, ^1D) states to the reactive cross-section [14]. The outcomes of this experiment were interpreted by quasi-classical calculations [15], deriving a rate constant of k (300 K) = 4.4×10^{-12} cm^3 s^{-1} for the charge transfer involving the ^3P state.

The results of all previous investigations will be discussed in Section 3 of the present paper. However, it is possible to point out some general observations concerning previous work: (i) in the majority of cases, state-selected information on the reactivity has been obtained only by using the state selective removal of Ar^{2+} by reaction with a buffer gas. The validity of this somehow "self-referential" approach has never been independently verified and (ii) for most of the neutral targets, no definitive results on Ar^{2+} (^1D) reactivity have been obtained.

In the last years, our research groups investigated the properties of doubly charged atomic and molecular systems: we studied dication thermodynamics [16,17], ion-molecule reactions involving dications [18–23], we measured internal energy effects in the reactivity of CO_2^{2+} [24] and, more recently, we investigated the dynamics of the double photoionization process producing N^{2+} from N_2 [25]. We also investigated the implications of our work for the modelling of planetary atmospheres [26,27].

The present paper reports on strong state-specific effects detected in the cross-section of charge transfer reactions between doubly charged ions Ar^{2+} and several neutral targets (He, Ne, Kr, Xe, D_2, and CH_4). In the experiment, the different Ar^{2+} states were populated by using tunable synchrotron radiation from two storage rings, Super-ACO (LURE-Paris) and ELETTRA (Sincrotrone Trieste, Trieste). State sensitivity was revealed by varying the photon energy from 43 to 52 eV and measuring the evolution of the absolute reaction cross-section. The study of multiple targets made it possible to investigate the details of the double ionization process of Ar atoms and to correlate specific reactivity with either the ground and/or the metastable states of the dication. No removal of ionic state is necessary in this case. Furthermore, assuming a statistical production of the three states, we estimate the state-selected cross-sections for the charge transfer processes and finally, using all the information, we extract an energy-dependent production branching ratio for the three dicationic states in the investigated energy range. This result is particularly interesting, since it allows identification of photon energy-dependent double ionization mechanisms towards the different final states. Such information at each photon energy would require time-consuming measurements of the two photoelectrons and of their kinetic energy in coincidence.

2. Experimental

Charge transfer cross-sections were measured using the CERISES [20,28] apparatus installed first at the undulator beamline SU6 of the Super-ACO storage ring (LURE-Paris) and, subsequently, on the branch line of the gas phase photoemission beamline at the ELETTRA synchrotron radiation facility (Trieste, Italy). The CERISES apparatus is a tandem mass spectrometer composed of two octopoles located between two quadrupole mass spectrometers in a *Q1-O1-O2-Q2* configuration (where *Q* stands for quadrupole and *O* for octopole) placed in three differentially pumped regions. Such a configuration permits investigation of both uni- and bi-molecular reactions of mass-selected ions. In the source region, Ar^{2+} ions were produced by double photoionization of Ar by synchrotron radiation. After ionization, ions were extracted from the source by a small field of 1 V/cm, and injected through a stack of electrodes into the quadrupole mass filter *Q1*. At the exit of this filter, ions were refocused into the *O1* radio frequency ion guide towards the reaction cell. Depending on the acceleration potential, the reactant ions produced in the source needed at most 40 μs to reach the reaction cell. Dication reactions took place in a 4-cm long scattering cell filled with the neutral target gas (He, Ne, Kr, Xe, D_2, and CH_4) at room temperature. The absolute value of their pressure was measured by a Baratron capacitance manometer and adjusted to a value ≈10^{-4} mbar to ensure single-collision conditions. The reactant ion kinetic energy is defined by the dc potential difference between the collision cell octopole and the center of the ion source. It can be varied between 0.4 and 40 eV in the laboratory energy frame, with a typical distribution width of 0.5 eV full width at half maximum (FWHM). Reactant and product ions were confined by the radio frequency guiding field of *O1*, guided by *O2*, mass selected in the *Q2* mass filter, and finally detected by a multichannel plate detector. Data were recorded according to a procedure described in Ref. [28]. The total electron yield resulting from Ar photoionization in the ion source was recorded during all measurements to correct for any variation of the Ar pressure. Photon energy scans, collecting ionic yields of Ar^{2+} and Ar^+ with and without the neutral target gas in the reaction cell permit to correct for any contribution to reactivity occurring outside the calibrated reaction cell [29]. Photoion signals were normalized to the incident photon flux as a function of photon energy. Effective absolute cross-sections (EACS, σ') were derived from the ratio of product to parent ion intensities and from absolute target gas pressure measurements. EACS are therefore absolute measurements of the reactivity of a mixture of ground and excited states. Provided monochromatic photons of selected energy were used, the relative population of these states is purely dependent on the energetics and the spectroscopy of the Ar^{2+} production. Conversely, if some higher order photons were emerging from the monochromator, they had the effect to perturb the population (e.g., by the production of excited states) and therefore led to a deviation from the rule mentioned above. For this reason, we used optimal higher order filtering while performing the measurements.

If the systematic uncertainty on the EACS is estimated to 25%, the random uncertainty is much lower, in the range of 5%. The