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Ion–ion coincidence experiments with low extraction fields

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ABSTRACT

The fragmentation of a polyatomic molecular dication has been investigated by means of a Monte Carlo simulation which can take into account realistic experimental conditions. The simulation applied to the three body process $CH_4^{2+} \rightarrow CH_2^+ + H^+ + H$ shows that the low angular acceptance, consequence of the low extraction field, does not prevent the distinction between the initial charge separation and the synchronous concerted decay mechanisms, which lead to the same final state. The comparison of the results with recent experiments [1] confirms that an initial charge separation with a following loss of a hydrogen atom describes better the experimental observations.

1. Introduction

Experiments where two or more charged fragments are detected via time coincidence techniques represent the most suitable approach to the investigation of the fragmentation of polyatomic molecular dications. In these experiments an ion pair or an ion pair in coincidence with an electron are detected. The goal is to identify the different fragmentation patterns depending on the dication state, to measure the energy and angular distributions of the fragments and to deduce the fragmentation mechanism. The technique introduced in the eighties with laboratory photon sources [2], largely benefitted by the development of lasers and synchrotron radiation [3,4], as well as position sensitive detectors [5,6]. The core tool for these experiments is represented by an ion Time-of-Flight (TOF) spectrometer, which, via the measurement of the time T_1 and T_2 needed for the fragments to reach the detector from the interaction region, allows the determination of their mass and their kinetic energy. The results are usually represented by two dimensional maps with the arrival times of the fragments on the axes. Correlated ion pairs result in features with shapes strongly dependent on the fragmentation process which generated them. This has been proved by a series of simulations which consider the full angular acceptance in the spectrometer [7–13]. A full angular acceptance is achieved in experiments where strong extraction fields (e.g. a few hundreds V/cm) are applied to the interaction region. However, experiments have also been performed with low extraction fields because they allow the measurement of the kinetic energy distribution of the ions with higher resolution [1,14–16]. The drawback in these latter experiments is the low angular acceptance. This might question the possibility to extract information on the fragmentation mechanisms, because only part of the features due to the correlated pair are observed in the (T_1, T_2) maps. Here we show with a realistic simulation that also with low extraction fields the different mechanisms leading to the fragmentation of a dication can be disentangled. As a case study we will use the three body reaction $CH_4^{2+} \rightarrow CH_2^+ + H^+ + H$ studied in Auger electron–ion [17], photoelectron–ion [7] as well as ion–ion coincidence experiments [1,18]. In particular the results of this simulation will be compared with the experimental data obtained in an Auger electron–ion–ion coincidence experiment. Thus in Section 2 the experimental apparatus used to collect this data is presented. In Section 3 the details of the simulation procedure are described, while the results of the simulations for the two different fragmentation mechanisms under consideration as well as the comparison with the experimental results are presented and discussed in Section 4. Finally some conclusions are collected in Section 5.

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2. Experimental

A detailed description of the experimental setup and procedures of the data collection have been reported elsewhere [19]. In the following only some details relevant to the present work are summarized. The vacuum chamber (base pressure $\leq 10^{-7}$ mbar) used for these experiments is equipped with two spectrometers: a Wiley-McLaren Time-of-Flight mass spectrometer (TOF-MS) for the detection of ions and a Cylindrical Mirror Analyzer (CMA) placed in front of the TOF-MS for the electron detection. A DC extraction field of 120 V/cm is applied to the interaction region to extract the ions. The CMA has an angular acceptance of $\pm 7^\circ$ around the angle $\phi = 42.7^\circ$. This results in an accepted geometrical solid angle of $\Delta\Omega = 1.53$ sterad. The electron energy resolution, $\Delta E/E$, is about 1.1%. This value is mainly determined by the size of the interaction zone which is about 0.1 and 2–3 mm, parallel and normal to the extraction field, respectively. With such an intrinsic energy resolution the presence of a DC field in the interaction region does not degrade the energy resolution of the Auger spectra measured by the CMA. The electron gun, has been operated at 4 keV incident energy and at a current $I \leq 1$ nA during the present measurements. The Auger electron–ion coincidence electronics is based on the use of a CAMAC time-to-digital converter (TDC LeCroy 4208), operated in a multihit configuration with a common start. The pulses of the channeltron multiplier mounted at the exit slit of the CMA, after being properly amplified, discriminated (Philips Scientific 704) and delayed (Philips Scientific 794) provide the common start for the TDC and the end of the time acquisition window (10 μs). The stop signals are provided by the pulses from the two Micro Channel Plates (MCP) mounted in the chevron configuration at the end of the TOF-MS. A personal computer governs the data acquisition via a CAMAC crate controller (CAEN C111), does a preliminary analysis and displays the Auger electron–ion coincidence on-line. The triple coincidence spectra are built *a posteriori*. The intensity of the incident electron beam and the density of the gas target (leading to ion and electron count rates of 120 kHz and 20 Hz, respectively) ensure an almost constant contribution of random coincidences over the full time spectrum investigated. In such conditions an accumulation time of about 100 h for each Auger electron–ion–ion coincidence map is needed.

3. Modeling and simulation

In the simulation we have adopted the following assumptions [20]: the precursor dication has no or negligible linear momentum with respect to the kinetic fragments and its lifetime is short enough to assure that the fragmentation occurs within the interaction region; the momenta associated with the two charged fragments are well defined once the energy available in the dissociation process has been defined; conservation of the linear momentum in the first and the second step of the dissociation holds; the directions of the fragments with respect to a fixed laboratory frame are randomly distributed (the target molecules are neither oriented nor aligned); the excitation source is unpolarized.

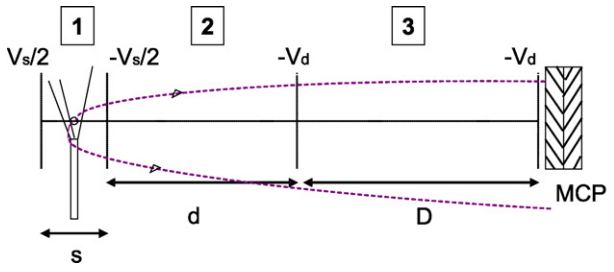

Fig. 1. Scheme of the TOF spectrometer used in the simulations. The labels 1, 2 and 3 correspond to the extraction, acceleration and field free zones, respectively. As an example, the trajectories of two ions with opposite initial momentum have been drawn (dashed line). In the simulation $s = 1$ cm, $d = 5.4$ cm, $D = 55.9$ cm as in Ref. [19].

The total TOF of each fragment ion from the center of the interaction region to the detector (Fig. 1), is the sum of three contributions associated with the three sections of the TOF spectrometer (named the extraction, the acceleration and the field free zones, labeled 1, 2 and 3, respectively):

$$T = t_1 + t_2 + t_3$$

$$t_1 = \frac{1}{a_1}\left[\sqrt{2a_1\left(\frac{s}{2} - x_0\right) + v_0^2\cos^2(\theta)} - v_0\cos(\theta)\right]$$

$$t_2 = \frac{1}{a_2}\left[\sqrt{2a_2\left(d - \frac{s}{2}\right) + 2a_1\left(\frac{s}{2} - x_0\right) + v_0^2\cos^2(\theta)} - \sqrt{2a_1\left(\frac{s}{2} - x_0\right) + v_0^2\cos^2(\theta)}\right]$$

$$t_3 = \frac{D - d}{\sqrt{2a_2(s/2 - x_0) + v_0^2\cos^2(\theta)}}$$

where m and q are the mass and charge of the fragment, and the accelerations in the extraction and acceleration zone, respectively, are defined as

$$a_1 = \frac{q(V_s - V_{x_0})}{m}, \quad a_2 = \frac{q(V_d - V_s)}{m(s/2 - x_0)}$$

where s, d and D are the length of the extraction, acceleration and field free regions, respectively. The angle θ between the direction of the ion and the axis of the spectrometer (our laboratory frame) is randomly distributed within the range 0–180° for the ICS (Initial Charge Separation) and 0–360° for the synchronous decay mechanisms. Due to the cylindrical symmetry of the setup in the simulation, there is no need to define other angles to explore all the possible orientations of the dication. V_s and V_d are the extraction and acceleration voltages, respectively. For the ion TOF spectrometer we assume the Wiley-McLaren prescriptions to achieve time focussing conditions [19,21] which link V_s and V_d once the geometrical parameters s, d and D are fixed. T is proportional to the projection of the initial momentum of the ion along the axis of the spectrometer, while the component perpendicular to the axis of the spectrometer is used to determine the probability that the ion hits the detector. In the simulations this is crucial: when the extraction field is not strong enough to bend all the trajectories towards the detector, the ions with a large component of the momentum perpendicular to the spectrometer axis are not detected. The interaction zone has been represented by a cylinder (100 μm diameter and 700 μm length). In the simulation the initial position, the energy and direction of the ion pairs were generated randomly. According to the assumptions made at the beginning of this section an isotropic angular distribution and a flat energy distribution of the ions have been considered. For each fragmentation mechanism fifty thousands trajectories have been computed.

4. Results

Let's consider the three body reaction $CH_4^{2+} \rightarrow CH_2^+ + H^+ + H$ studied in [1]. In those experiments the dication was formed via inner shell ionization followed by Auger electron decay and the CH_2^+/H^+ ion pair was measured in coincidence with an Auger electron, which allows the selection of the initial dication state. To discuss in detail the mechanisms leading to the fragmentation a proper definition of the sequence of events occurring is needed. The nomenclature proposed by Maul and Gericke [22] points to the *time dynamics* of the process using terms like synchronous, asynchronous and sequential fragmentation, while that of Eland [23],