

**FRAGMENTATION OF H₂O AND CH₄ MOLECULES INDUCED BY
650 KEV N⁺ PROJECTILES****S.T.S. Kovács^{1,2}, P. Herczku^{1,2}, Z. Juhász¹, B. Sulik¹**¹MTA Institute for Nuclear Research, 4026 Debrecen, Bem ter 18/c²University of Debrecen, 4032 Debrecen, Egyetem ter 1.**Abstract**

Ion induced fragmentation of H₂O and CH₄ molecules by 46 keV/u N⁺ projectiles was investigated. The energy and angular distribution of the fragments has been measured with an energy dispersive electrostatic spectrometer. Single differential fragmentation cross sections of the emitted fragments have been determined, and multiple ionization cross sections for the target molecule were obtained. The maximum observed degree of ionization was 5 and 4 for water and methane molecules respectively.

I. Introduction

Dissociation of small, few-atomic molecules has extensively been studied. Numerous experiments were carried out with photon [1], electron [2] and ion [3] projectiles on different target molecules, in order to understand the fundamental physics of fragmentation processes, which have major importance not only in atomic- and astrophysics but in several applied fields such as industrial applications and radiotherapy. For the latter field, the most important projectile energy region is the Bragg-peak, where the Linear Energy Transfer (LET) reaches its maximum. However, the fragmentation yield only weakly follows the curvature of the Bragg-peak: the yield is more flat than it is expected [4]. In spite of that finding, the commonly used radiotherapy is based mainly on LET: the maximum of the LET is set exactly to the volume where the tumor is located. Experimentally obtained excitation, ionization and fragmentation cross sections are integrated into the treatment planning

nowadays, and there are also attempts in the theoretical description of radiation induced molecular damages [5]. It is important to note here that the degree of ionization of heavier ion projectiles is typically 0, 1 or 2 in the Bragg peak region. Our aim is to study the fragmentation process with medium energy, low charge state projectiles, close to the case of carbon-ion therapy. The single charged nitrogen ion is a good candidate for such studies.

From the physics point of view, ion induced molecule fragmentations are very complex processes. When a charged particle interacts with a target molecule, several excited and ionized states of the transient molecular ion can be produced, depending on the energy transfer to the target. The simplest quantity which governs the collision is the interaction strength (Sommerfeld parameter $k=Q/v$) [6]. It depends only on the charge (Q) and velocity (v) of the projectile ion. At small k values ($k \ll 1$) the target is only slightly perturbed by the projectile, while at high k values ($k \gg 1$) the projectile strongly interacts with the target. Our measurements are specific in the sense that for the ionic charge of the projectile fall into the weak interaction region ($k \ll 1$). Here the most probable ionization process is the direct, single ionization. However, for heavy ions the interaction can be much stronger in closer collisions, where the projectile electron cloud does not screen its nuclear charge. Therefore, multiple ionization is more important here than for protons with the same velocity.

By the collision the target molecule can be excited to one of the several possible excited or ionized states. These states may decay with relaxation or fragmentation. The products of the dissociation can be excited or ground state fragments. There are also two or three-step fragmentation processes such as $H_2O^{2+} \rightarrow OH^+ + H^+ \rightarrow O^+ + H^+ + H^0$. Those fragments which comes from the dissociation of a singly charged molecular ion have very low kinetic energies (0 - 2 eV), while the fragments originating from doubly and multiply charged ($q \geq 2$) transient molecular ions have higher kinetic energies ($\gg 1$ eV) due to the Coulomb-repulsion between the charge centers (Coulomb-explosion). Hence, the total kinetic energy (KER) of the fragments is increasing with the increasing charge state of the transient molecular ion.

From the biological point of view the above mentioned physical processes are only the first few steps of that extremely complex sequence of events which finally lead to cell death [5]. Numerous chemical reactions and biological mechanisms contribute to DNA damages or act against that, which are intensively studied nowadays. The time scale of these secondary processes covers a wide range from 10^{-22} s to minutes or even longer times.

II. Experiment

The experimental setup is practically identical to that described in Ref. [7]. Here we provide only a brief description of the method.

Jets of water vapor and methane gas were formed by an effusive molecular gas target system [8]. Nitrogen ion projectiles with energy of 650 keV were provided by the VdG-5 accelerator in Atomki. The charged particles, ejected from the reaction region were angle and energy analyzed by an energy dispersive electrostatic spectrometer [9], fixed on a rotatable ring. The typical pressure in the experimental chamber was cca. 10^{-6} mbar without target gas injection and around $1 \cdot 10^{-5}$ mbar during the measurements.

III. Results and discussions

According to data from the literature [10, 11] we identified the fragmentation channels for both H₂O (see Figure 1) and CH₄ targets. In the fit, the initial energy parameters of the individual Gaussian peaks were taken from the available data from theories and earlier experiments [10, 11]. In most cases, the peak positions were not significantly modified by the fit. The ratio of the peak energy and width appeared to float around a constant value (~ 2 in the case of water and $\sim 2,5$ for methane), which resulted in increasing FWHM of the peaks as the energy increased. Some sharp structures also appeared in the spectra (see for example peak group 3 in figure 3). Principally in the case of methane there were several closely lying peaks that we were not able to fit separately. In these cases we used only 1 or 2 Gaussian curves to cover the structure.

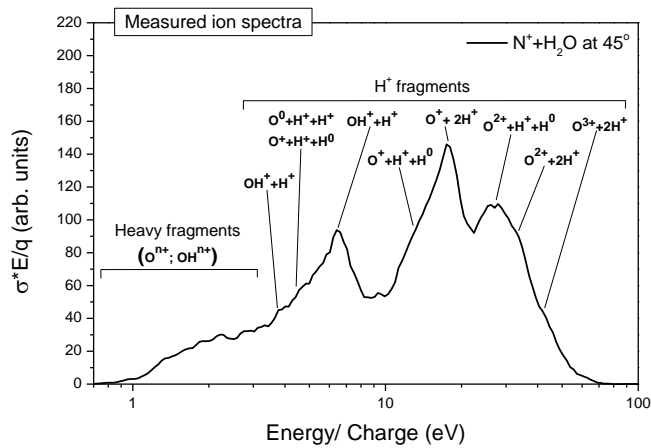


Figure 1: Measured water fragmentation spectrum and peak identification. Heavy fragments appear below 3 eV. The peaks above 3 eV are from protons originating from the indicated fragmentation channels.

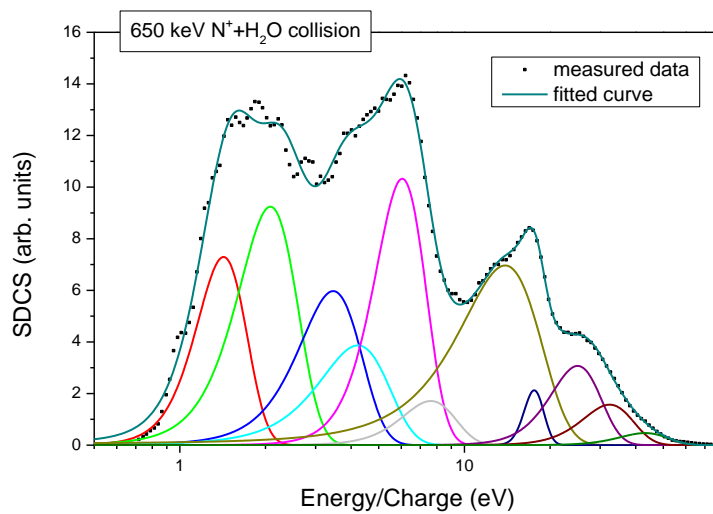


Figure 2: Single differential fragmentation cross section for H_2O and the fit results. The 2 peaks below 3 eV are “collector” peaks for heavy fragments from all fragmentation channels. Peaks above 3 eV are due to protons.

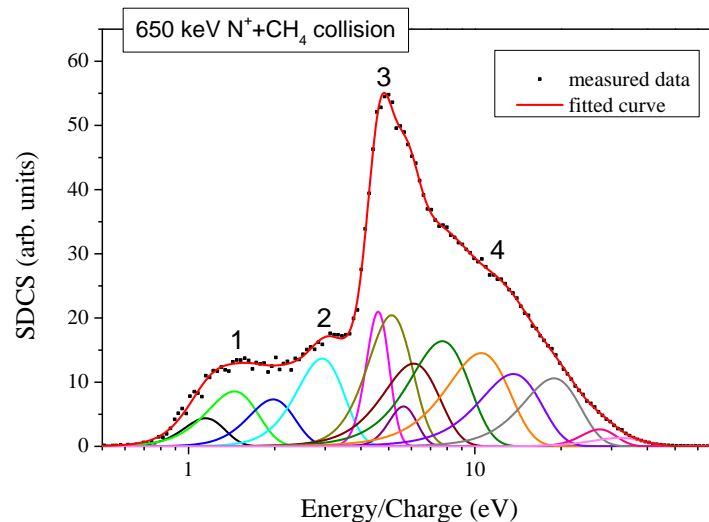


Figure 3: Single differential fragmentation cross section for CH_4 and fit results: peak group 1 (between cca. 1 and 2 eV) contains mostly heavy fragments (C^q+ ; CH_n^{q+}); peak group 2 (around 3 eV) belongs to H_2^+ fragments; peak group 3 is a complex, sharp structure containing H^+ fragments from several fragmentation channels of the CH_4^{2+} molecular ion; peak 4 is a wide, complex bump due to protons originating from the fragmentation of multiply charged molecular ions.

From our fit results (see Figure 2 and 3) we determined the relative yields of the different fragmentation channels. Then, from the yield of the light fragments (H^+) we obtained the relative double and multiple ionization probabilities for both target molecules (Table 1). It is important to mention here that, these ionization probabilities contain only those ionization events which finally lead to the fragmentation of the molecule. Single ionization cross sections cannot be determined with the present method. Mostly, because the fragmentation rate of single ionized molecules is less than unity. Partly, because fragment energies from the ion+neutral channels overlap with those of the heavy fragments originating from ion-pair breakups. Finally, we arrive to the limits of energy dispersive spectroscopy here. With our setup, the method cannot be considered to provide quantitative results below 2 eV.

Table 1: Relative double and multiple ionization probabilities (yields) of H₂O and CH₄ molecules with the related fragmentation channels.

Degree of ionization (H ₂ O ^{q+})	Relating channels	Yield	Degree of ionization (CH ₄ ^{q+})	Relating channels	Yield
q=2	OH ⁺ +H ⁺ O ⁰ +H ⁺ +H ⁺ O ⁺ +H ⁺ +H ⁰	142,12	q=2	CH ₃ ⁺ +H ⁺ CH ₂ ⁺ +H ⁺ +H ⁰ C ⁺ +H ⁺ +neutral	388,13
q=3	O ⁺ +H ⁺ +H ⁺ O ²⁺ +H ⁺ +H ⁰	46,50	q=3	CH ₂ ⁺ +H ⁺ +H ⁺ CH ₃ ²⁺ +H ⁺	139,41
q=4	O ²⁺ +H ⁺ +H ⁺	25,97	q=4	CH ₂ ²⁺ +H ⁺ +H ⁺	22,48
q=5	O ³⁺ +H ⁺ +H ⁺	9,96			

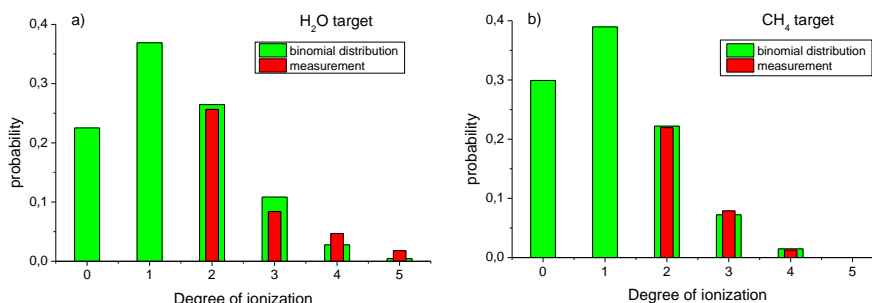


Figure 4: Fit of the relative yields with binomial distributions. Green columns are the terms of the binomial distribution, using the probabilities $p_a=0.165$ and $p_b=0.140$ for water and methane respectively. The red columns are the measured yields, proportional to the ionization probability.

Binomial distributions are often used to characterize events which are independent from each other. In our measurements we found that the

probabilities of double and multiple ionizations do not follow perfectly the binomial distribution: in the case of water, this binomial fit distribution highly underestimates the multiple ionization probabilities, while for methane the agreement is much better. These differences from the binomial distribution are most likely due to the electron correlation in the molecule. Another possible reason of the discrepancy could be the consequence of the “dressed up” single charged projectile. The effective charge of the projectile is different at different impact parameters. In close collision events the effective charge may highly exceed the ionic value, which results multiple ionizations with a relatively high probability. Of course at high impact parameters the ionization probability depends also on the orientation of the molecule. In distant collisions the effective charge is $q=1$ (in our case), where single ionizations are the most probable ionization processes. In our experiments we measure differential cross sections, which involve both high and low impact parameter events, the results will be a mixture of close and distant collisions.

IV. Conclusions

We investigated the fragmentation of water and methane molecules. Relative ionization probabilities of the target molecules were obtained from the yields of the related fragmentation channels (see Table 1).

The ionization yield of H_2O and CH_4 monotonically decreases with increasing degree of ionization. In the case of methane the yield of the different ionization states are close to the binomial distribution, while for water, the binomial fit extremely underestimates the probabilities of multiply ionizations. It is important to mention these ionization probabilities contain only those ionization events which finally lead to the fragmentation of the molecule. While at lower ionization degrees the investigated target molecules often dissociate into two fragments, at higher ionization states ($q \geq 3$) the molecules clearly prefer to dissociate into three (or more) charged fragments (see for example figure 1).

Further measurements and theoretical investigations are planned.

Acknowledgement

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