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# The role of internal energy of polyatomic projectile ions in surface-induced dissociation

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Received 29 April 2003; in final form 5 June 2003

Published online: 9 July 2003

## Abstract

The effect of initial internal energy on the extent of surface-induced fragmentation was investigated in a tandem mass spectrometer for  $\text{CH}_3^+$  and  $\text{CH}_4^+$  ions prepared in different ion sources. The different initial internal energy content had a considerable effect on the extent of fragmentation of the surface-excited projectile ions: ions from a Nier source with a large amount of initial internal energy fragmented at much lower collision energies than internally relaxed projectile ions from a Colutron source. A quantitative estimation of this effect showed that the initial internal energy content of the projectile ions was entirely preserved in the projectile ion during the ion/surface collision.

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## 1. Introduction

Interactions of ions with surfaces have been used to characterize both the gaseous ions and the surfaces [1,2]. Ion surface reactive collisions is an area which has been rapidly growing the past years in an effort to explore and develop new methods for characterizing the properties of gaseous ions

and to investigate the basics of the ion/surface interaction. Besides physical and chemical sputtering, interest has been concentrated in particular on low-energy (in the range of tens of eV) collisions involving surface-induced dissociation (SID) and surface-induced reactions (SIR). In addition, to its intrinsic interest, ion surface reactions are also relevant for a number of technological applications including such different fields as secondary mass spectrometry, plasma processing (production of advanced materials), reactions of ions with aerosols in the Earth's atmosphere and in interstellar medium [3] all the way to plasma-wall interactions in electrical discharges and fusion plasmas [4]. Much of the modelling and diagnostics of plasmas

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relies on the understanding of the atomic and molecular processes which occur in the plasma and at the plasma wall.

For instance it turned out that the use of low-Z wall materials such as carbon, boron and beryllium has been beneficial in present large tokamaks [5]. In ITER design [6], graphite-based low-Z material (with its high-thermal resistivity) is recommended for divertor plates and first wall protection for the initial operation phase, in order to minimize the risk of plasma contamination. For instance, energetic plasma particles strike solid surfaces such as limiters and divertors of a tokamak vessel, thereby eroding the surface material by chemical and physical (sputtering) reactions. Charged and neutral particles emitted from the surface may interact with the plasma and hit the surface again. The available databases on plasma–surface interaction mainly include data on physical and chemical sputtering/erosion, material deposition and hydrogen/deuterium recycling. Less reliable data are known on fragmentation and chemical reactions during molecular ion scattering at these walls [4]. These data have so far been limited to laboratory studies mainly involving  $H^+$  and  $O^+$  projectiles [7] and small ions (see the references given in [8]), and only recently extended to systems such as  $CH_3^+$  and  $CH_4^+$ , but with conflicting results [8–12]. Sugai and co-workers [8,9] using the hydrocarbon projectile ions  $CH_4^+$ ,  $CH_3^+$  and  $CH_2^+$  produced in an inductively coupled magnetically confined plasma source with energy distributions with a FWHM of about 15 eV were the first to report mass spectra of ions scattered from an aluminum surface. They observed strong fragmentation even at very low-collision energies (all the way down to about 0 eV collision energy) observing not only  $CH_2^+$  and  $CH^+$  product ions from  $CH_3^+$  projectile ions, but also  $C^+$  and  $H^+$  fragment ions. In contrast, exploratory studies in our own laboratory [10] using ions from a dc gas discharge ion source (Colutron) did not show any sign of fragmentation when interacting these ions (at energies up to about 50 eV) with a hydrocarbon-covered stainless steel surface. Nevertheless, follow up studies using hydrocarbon ions from a Nier-type electron impact ion source in our laboratory [12] and in the laboratory of Herman and

co-workers [11] did again show considerable fragmentation, but no signs of atomic fragment ions.

The surface collision of a polyatomic ion has been characterized as a multi-mode excitation process in which energy is exchanged between surface modes and polyatomic projectile ion modes. A number of investigations [1,2,13–26] have dealt with the question how efficient is this energy exchange, i.e., how is the initial kinetic energy partitioned to surface energy, internal energy and translational energy of the product ions. The least addressed problem so far appears to be the role of the initial internal energy of the polyatomic projectile,  $E_{int}$ , in the fragmentation of the surface-excited projectile ion. For instance, is the initial energy content fully randomized between the surface modes and internal modes of the projectile ion, or is it at least partly retained within the projectile ion and thus influences the subsequent dissociation processes after the surface collision?

In order to address this question and in particular to resolve the above mentioned contradictory results for surface-induced dissociation of the  $CH_3^+$  and  $CH_4^+$  ions, we carried out here a systematic series of experiments on surface dissociation for these simple polyatomic hydrocarbon projectile ions, prepared with different internal energy content using different ion sources where projectile ions are on the one hand formed by electron impact ionization and on the other hand by ion–molecule reactions.

## 2. Experimental

Experiments were carried out with the tandem mass spectrometer apparatus BESTOF described in detail in earlier papers [18,26]. It consists of a double-focusing two-sector-field mass spectrometer (reversed geometry) combined with a linear time-of-flight mass spectrometer. Projectile ions were produced either in a low-pressure Nier-type electron impact ion source or at elevated pressures in a Colutron gas discharge source.

The ions produced were extracted from the ion source region and accelerated to 3 keV for mass (and energy) analysis by a double-focusing two-

sector-field mass spectrometer. After passing the mass spectrometer exit slit, the ions were refocused by an Einzel lens and decelerated to the required collision energy by a system of deceleration lenses before interacting with the target surface. Shielding the target area with conical shield plates minimized field penetration effects. The incident impact angle of the projectile ions was kept at  $45^\circ$  and the scattering angle (defined as a deflection from the incident beam direction) was fixed at  $91^\circ$ .

The collision energy of ions impacting on the surface is defined by the potential difference between the ion source and the surface. The potential difference (hence, the collision energy) can be varied from about zero to about 2 keV with a typical resolution of about 200 meV (full width at half maximum) in the case of the Nier-type ion source and of about 1 eV in the case of the Colutron-type ion source.

A fraction of the product ions formed at the surface exited the shielded chamber through a 1 mm diameter orifice. The ions were then subjected to a pulsed extraction-and-acceleration field that initiated the time-of-flight analysis of the ions in the second mass analyzer. The mass selected ions were detected by a double-stage multi-channel-plate, connected to a multi-channel scaler (time resolution of 5 ns per channel) and a laboratory computer. The product ion intensities were obtained by integration of the recorded mass spectral ion signals (see mass spectra in Fig. 1) thereby removing instrumental effects.

The Nier-type source was a commercial CH5VarianMAT mass spectrometer source [27] operated at pressures of about  $10^{-5}$  Torr. Ions were prepared by impact of 120 eV electrons on methane thereby producing the presently studied projectile ions  $\text{CH}_3^+$  (as a fragment ion) and  $\text{CH}_4^+$

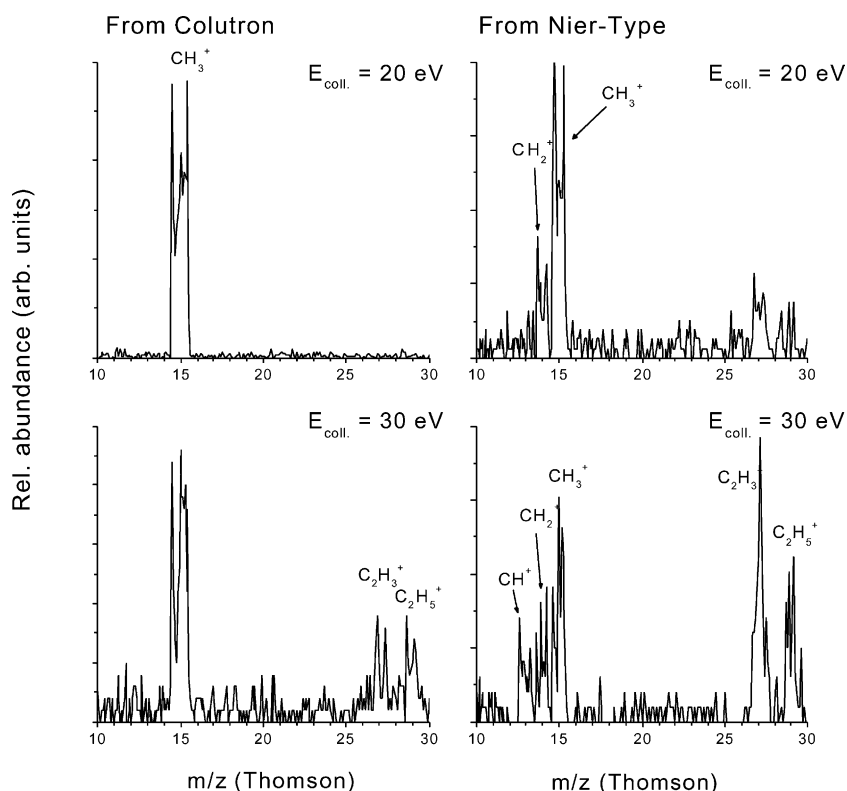


Fig. 1. Secondary mass spectra of product ions produced in collisions of  $\text{CH}_3^+$  with a hydrocarbon-covered stainless steel surface at collision energies of 20 and 30 eV. Spectra on the left side:  $\text{CH}_3^+$  from the Colutron source; spectra on the right side:  $\text{CH}_3^+$  from the Nier-type source.

(as a parent ion). The ion source was operated at an elevated temperature of about 100–200 °C. The Colutron source was operated with a 9:1 hydrogen:methane mixture at a pressure of 0.2–0.5 Torr. The main process is evidently ionization of hydrogen and subsequent charge transfer between hydrogen ions and methane; a variety of hydrocarbon ions of  $C_1$ ,  $C_2$  and  $C_3$  groups are then formed by successive ion–molecule reactions including the presently studied projectile ions  $CH_3^+$  and  $CH_4^+$ .

The surface used here was a polished stainless steel surface maintained under ultrahigh vacuum conditions ( $10^{-9}$  Torr) in a bakeable turbo-pump evacuated target collision chamber. However, even these conditions did not exclude deposition of multi-layers of hydrocarbon contaminants on the surface, whenever the valve between the mass spectrometer and the target collision chamber was opened and the pressure in the target region increased to the  $10^{-8}$  Torr range. The surface was thus a hydrocarbon-covered metal surface as in our earlier studies, thereby mimicking a ‘real’ surface as occurring in many situations dealing with plasma–wall interactions in low- and high-pressure and low- and high-temperature plasmas.

### 3. Results

Fig. 1 shows the product ion mass spectra obtained at collision energies of 20 and 30 eV for the projectile ion  $CH_3^+$  produced in the Colutron and the Nier-type ion source, respectively. With  $CH_3^+$  formed in the Colutron source (Fig. 1 left side) only  $CH_3^+$ , and the reaction products  $C_2H_3^+$  and  $C_2H_5^+$  were observed over the collision energy range up to 60 eV. The latter two  $C_2$ -group ions were shown earlier [11,12] using the same surface and deuterated molecular projectile ions to result partly from surface chemical sputtering reactions and partly by chemical reactions of the projectile ion with terminal  $CH_3$ -groups of surface hydrocarbons. Surface-induced chemical reactions (SIR) and surface chemical sputtering are not the subject of this Letter and will not be discussed further here. Evidently, however, no surface-induced dissociation (SID) of the projectile  $CH_3^+$  formed in

the Colutron ion source was observed over the entire collision energy region investigated (i.e., up to 60 eV). The situation is quite different for  $CH_3^+$  formed in the Nier-type source (Fig. 1, right side). With increasing collision energy, the  $CH_3^+$  projectile ion shows dissociation to  $CH_2^+$  and  $CH^+$ . Also here product ions  $C_2H_3^+$  and  $C_2H_5^+$  are formed partially as a result of surface sputtering and partially as a result of the surface chemical reaction. The data in Fig. 1 (right size) are in good agreement with the data in [11,12] using electron impact ionization to produce the projectile ions and the data in Fig. 1 (left side) in good agreement with the preliminary data in [10] using a Colutron source.

Fig. 2 summarizes the data on surface-induced dissociation of  $CH_3^+$  in the form of collision-energy resolved mass spectrum curves (CERMS) for  $CH_3^+$  produced in the Nier-type ion source. The fragment ions  $CH_2^+$  and  $CH^+$  have their thresholds at about 15 and 22 eV, respectively. A comparison of the SID data for  $CH_3^+$  prepared in the two different ways clearly indicates that the projectile ions from the Nier-type ion source show a completely different behavior than those from the Colutron-type ion source. As will be demonstrated in detail below the ions from the Nier-type ion source have a considerably higher internal energy content than those from the Colutron source and it is this difference in internal energy content which manifests itself dramatically in the extent of the projectile ion fragmentation at comparable collision energies.

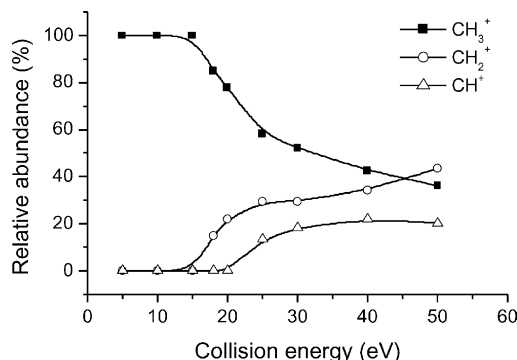


Fig. 2. Collision-energy resolved mass spectrum (CERMS curves) for  $CH_3^+$  projectile ions from the Nier-type source. Only product ions of surface-induced dissociation are shown.

The corresponding CERMS curves for product ions formed in surface-induced collisions of the  $\text{CH}_4^+$  projectile ion, formed either in the Colutron source or in the Nier-type source, are shown in Fig. 3. In both cases, dissociation of the  $\text{CH}_4^+$  projectile ion to  $\text{CH}_3^+$ ,  $\text{CH}_2^+$ , and at higher collision energies to  $\text{CH}^+$  can be observed. Nevertheless, in case of the  $\text{CH}_4^+$  from the Nier-type source, the dissociation processes start at much lower collision energies, shifted by about 30–35 eV, in comparison with  $\text{CH}_4^+$  from the Colutron ion source. Moreover, the product ion  $\text{CH}_3^+$  is more abundant for the projectile ions formed in the Nier source (55% for collision energies above 30 eV) as compared for ions in the Colutron source (25% for collision energies above 30 eV). It was shown earlier in studies of  $\text{CD}_4^+$ /surface collisions [11,12] that this ion was partly formed in a chemical reaction of the reactive radical  $\text{CH}_4^+$  projectile ion with hydrogen containing molecules on the surface yielding  $\text{CH}_3^+$  which subsequently dissociated to  $\text{CH}_3^+ + \text{H}_2$ . Our

present studies involving  $\text{CD}_4^+$ /surface collisions, with  $\text{CD}_4^+$  formed in the Nier source, lead to the same conclusion, i.e., at collision energies above 20 eV about half of the product ions result from direct projectile dissociations of  $\text{CD}_4^+$  to  $\text{CD}_3^+$  and about half from surface chemical reaction (leading to  $\text{CD}_4\text{H}^+$ ) followed by dissociation of the primary reaction product  $\text{CD}_4\text{H}^+$  to  $\text{CD}_2\text{H}^+ + \text{HD}$ .

#### 4. Discussion

Results displayed so far for the fragmentation of  $\text{CH}_4^+$  and  $\text{CH}_3^+$  projectile ions clearly indicated that there is a different fragmentation behavior for the projectile ions formed in the two different ion sources. This different fragmentation behavior must be related to different properties and one obvious property different for these two categories of projectile ions is their internal energy content. Thus in the following an attempt will be made to estimate quantitatively this internal energy from general information available on the two different production routes.

In the case of the low-pressure Nier-type ion source the projectile ions originate by electron impact ionization of the neutral molecule and possible subsequent unimolecular dissociation of the excited parent ion. Therefore, their internal energy content can be estimated from the break-down pattern of the respective molecular ion and knowledge on the photoelectron spectrum of the particular molecule (for more details see also [14,20,28]). The break-down pattern specifies the range of excitation energies of the molecular ion over which a particular ion is stable, and the photoelectron spectrum indicates the probability of deposition of a certain excitation energy into the molecular ion during the Franck–Condon governed ionization process. It is assumed in this estimation that the impact of electrons of energies above 70 eV leads to the same energy deposition as photon impact, i.e., autoionization processes are neglected. The internal energy distribution of a non-fragmenting molecular ion,  $P(E_{\text{int}})_M$ , is then given by

$$P(E_{\text{int}})_M = I_{\text{NM}}(E_{\text{int}})W_{\text{ph}}(E_{\text{exc}}), \quad (1)$$

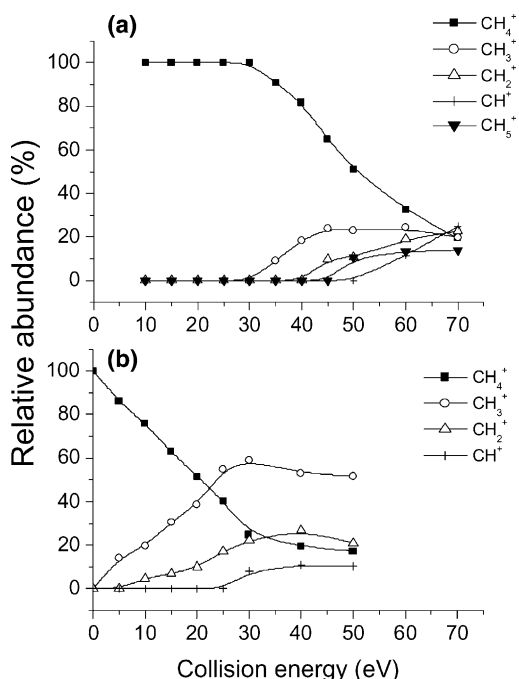


Fig. 3. Collision-energy resolved mass spectra (CERMS curves) for  $\text{CH}_4^+$  projectile ions from the Colutron source (a) and from the Nier-type source (b).

where  $I_{\text{NM}}(E_{\text{int}})$  is the normalized intensity of the molecular ion in the break-down pattern at the internal energy  $E_{\text{int}}$ ,  $W_{\text{ph}}(E_{\text{exc}})$  is the probability of depositing an excitation energy  $E_{\text{exc}}$  in the molecular ion as given by the photoelectron spectrum, and  $E_{\text{exc}} = E_{\text{ph}} - \text{IE}$  ( $E_{\text{ph}}$  is the photon energy and IE is the ionization energy of a molecule). For fragment ions an analogous equation is valid

$$P(E_{\text{int}})_{\text{F}} = I_{\text{NF}}(E'_{\text{int}})W_{\text{ph}}(E'_{\text{exc}}), \quad (2)$$

where  $E'_{\text{exc}} = A(E_{\text{ph}} - \text{AE})$ , where AE is the appearance energy of the fragment ion, and  $A$  is a correction factor which takes into account that the initial excitation energy of the molecular ion is statistically distributed over the integral degrees of freedom of the ion and neutral fragment formed. This correction factor expands the internal energy scale by  $1/A = (3N_{\text{M}} - 6)/(3N_{\text{F}} - 6)$ , where  $N_{\text{M}}$  and  $N_{\text{F}}$  is the number of atoms in the parent and fragment ion, respectively.

In Fig. 4 we show the internal energy for  $\text{CH}_4^+$  and  $\text{CH}_3^+$  formed by electron impact ionization of methane using these considerations. The figure gives in the top panel the break-down pattern of the molecular methane ion [29,30] and the photoelectron spectrum of methane [31] and in the lower two panels the  $P(E_{\text{int}})$  derived for  $\text{CH}_4^+$  and  $\text{CH}_3^+$ . It becomes immediately apparent that most of the  $\text{CH}_4^+$  and  $\text{CH}_3^+$  ions formed by electron impact in the low-pressure Nier-type source contain an appreciable amount of internal energy. For instance the average internal energy,  $(E_{\text{int}})_{\text{av}}$ , for  $\text{CH}_4^+$  is about 1.0 eV and it extends up to 1.8 eV, and for  $\text{CH}_3^+$  we estimate by extrapolation that the maximum of the internal energy is at least 2.3 eV (due to lack of more accurate data for the curves shown in the top panel of Fig. 4 it is not possible to give a more accurate estimate).

Estimation of the internal energy of projectile ions formed in the Colutron source is more difficult. In the 9:1 hydrogen to methane mixture used here at pressures of 0.2–0.5 Torr, the major ionization reactions in the gas discharge volume will be most likely electron impact ionization of hydrogen molecules and subsequent charge transfer between hydrogen ions and methane. This  $\text{CH}_4^+$  ion can react further to  $\text{CH}_5^+$  and in the mixture other hydrocarbon ions can be formed by succes-

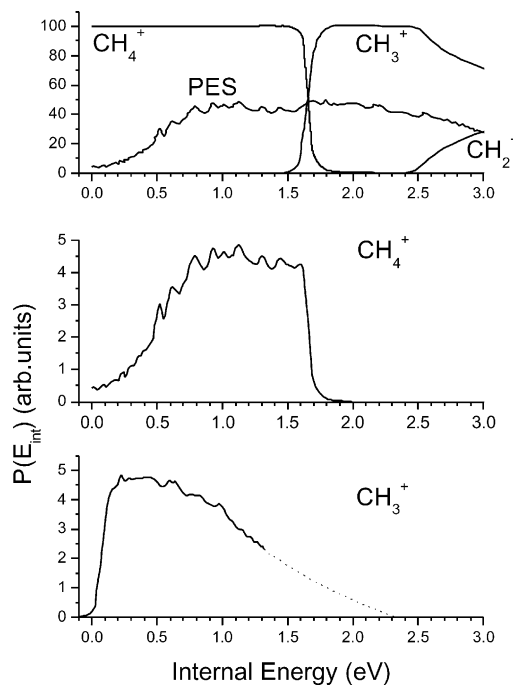


Fig. 4. Internal energy distribution  $P(E_{\text{int}})$  of the projectile ions  $\text{CH}_4^+$  and  $\text{CH}_3^+$  (produced by electron impact ionization of methane in the Nier-type source) estimated from the known photoelectron spectrum for  $\text{CH}_4$  and the break-down graph for  $\text{CH}_4^+$  (see text). Upper panel: photoelectron spectrum of methane (PES) after [31] and break-down curves after [29,30] of the methane molecular ion. Middle panel: estimated  $P(E_{\text{int}})$  of the molecular ion  $\text{CH}_4^+$ . Lower panel: estimated  $P(E_{\text{int}})$  of the fragment ion  $\text{CH}_3^+$ . Dashed line indicates extrapolated part of  $P(E_{\text{int}})$  for  $\text{CH}_3^+$  beyond the range of available data from the upper panel.

sive chemical reactions. However, all of these ions can relax their internal energy in non-reactive collisions with surplus hydrogen and methane and thus a plausible conclusion is that most of the projectile ions from the Colutron source are considerably relaxed ions, i.e., with internal energies close to zero.

With this in mind, in the following an attempt will be made to estimate the effect of the internal energy to the SID process quantitatively. For instance, the observed appearance thresholds in the collision energy dependence should in principle correspond to those ions containing the maximum possible initial internal energy, i.e., in the case of ions from the Colutron the necessary dissociation

energy at the threshold will be only supplied by translational energy transferred into internal energy during the surface collision, whereas in the case of ions from the Nier source additional energy will be available due to the initial internal energy. Thus values for these appearance energies and shifts in these values may be used to characterize possible internal energy differences.

The thermochemical thresholds for dissociation of  $\text{CH}_3^+$  into  $\text{CH}_2^+ + \text{H}$  and  $\text{CH}^+ + \text{H}_2$  are about 5.3 and 5.4–5.7 eV, respectively [32]. The average value of translational-to-internal energy transfer on hydrocarbon-covered metal or carbon surfaces has been well established in previous investigations [14,17,20,22,23,25,26] amounting to about 6% of the collision energy with an effective width of about  $\pm 1.5$  eV. It is thus not surprising that the appearance threshold of the  $\text{CH}^+$  curve is shifted by approximately 5 eV upward with respect to the  $\text{CH}_2^+$  in the CERMS plot in Fig. 2 (pertaining to the Nier-type ion source case) as this difference amounts approximately to  $5 \times 0.06 = 0.3$  eV energy transferred from collisional to internal energy and thus supplies the additional energy necessary when going from the threshold necessary for dissociation of  $\text{CH}_3^+$  to  $\text{CH}_2^+ + \text{H}$  to the threshold for dissociation of  $\text{CH}_3^+$  to  $\text{CH}^+ + \text{H}_2$ .

Moreover, the observed threshold for the occurrence of the  $\text{CH}_2^+$  fragment ion at about 15 eV collision energy can be interpreted as evidence for an appreciable amount of initial internal energy in the  $\text{CH}_3^+$  projectile as this collision energy only amounts to approximately  $15 \times 0.06 = 0.9$  eV internal energy transferred. Taking into account that the effective width of this energy transferred is  $\pm 1.5$  the necessary difference to the threshold value of about 5.3 can be accounted nicely by assuming that the  $\text{CH}_3^+$  ion produced in the Nier-type ion source has a maximum initial energy of at least 2.3 eV (see Fig. 4).

In contrast, the fact that ions from the Colutron ion source do not show any fragmentation in the present experimental energy window of up to 60 eV can be easily accounted for as in this case the whole energy for the dissociation process must be supplied by the surface collision (assuming no initial internal energy content prior to the collision), i.e., at a collision energy of 60 eV the max-

imum energy transferred is  $60 \times 0.06 = 3.6$  eV, this value being still below the thermochemical threshold value of about 5.3 eV. Thus the  $\text{CH}_3^+$  data are consistent with the hypothesis that the projectile ion  $\text{CH}_3^+$  from the Colutron source has only a very small internal energy, while that one from the Nier-type source has a rather large internal energy and this energy needs to be fully used as additional energy to drive the SID reaction.

Thermochemical thresholds for dissociation processes of  $\text{CH}_4^+$  into  $\text{CH}_3^+ + \text{H}$  and  $\text{CH}_2^+ + \text{H}_2$  are 1.7 and 2.5 eV, respectively [32,33] (see also the thresholds shown in the top panel in Fig. 4). In the case of  $\text{CH}_3^+$  the difference in the necessary threshold energies  $2.5 - 1.7 = 0.8$  can be directly related to an upward shift of the  $\text{CH}_2^+$  curve by approximately 10 eV with respect to the  $\text{CH}_3^+$  in the CERMS plots of Fig. 3 (in particular in the upper panel where the data for the Colutron source are shown). This shift amounts approximately to  $10 \times 0.06 = 0.6$  eV energy transferred from collisional to internal energy and thus supplies the additional energy necessary when going from the threshold necessary for dissociation of  $\text{CH}_4^+$  to  $\text{CH}_3^+ + \text{H}$  to the threshold for dissociation of  $\text{CH}_4^+$  to  $\text{CH}_2^+ + \text{H}_2$ . In the case of the CERMS plot for the Nier ion source (see the lower panel) this is not so clear due to influences of initial internal energy.

Moreover, the observed threshold for the occurrence of the  $\text{CH}_3^+$  fragment ion at about 30 eV collision energy in the upper panel of Fig. 3 (Colutron case) can be easily accounted for as in this case the whole energy for the dissociation process must be supplied by the surface collision (assuming no initial internal energy content prior to the collision), i.e., at a collision energy of 30 eV the maximum energy transferred is  $30 \times 0.06 = 1.8$  eV in nice accordance with the thermochemical threshold value of 1.7 eV. Conversely, in the case of the Nier-type source virtually the whole energy for dissociation can be supplied by internal energy (according to Fig. 4 the maximum energy content in the  $\text{CH}_4^+$  can reach about 1.8 eV) and thus as shown in Fig. 3 in the lower panel the  $\text{CH}_3^+$  fragment ion signal starts right at zero collision energy and the  $\text{CH}_2^+$  signal somewhat higher.

Instead of using these threshold values, we could consider the shifts of these thresholds in the



CERMS curves when going from Colutron produced to Nier-type ion source produced  $\text{CH}_4^+$  (see Fig. 3). For the product ion  $\text{CH}_3^+$  this amounts to a shift of approximately 30 eV and for  $\text{CH}_2^+$  approximately  $(40 - 5) = 35$  eV. This implies an average difference in translational-to-internal energy transfer (6% of the collision energy,  $0.06E_{\text{tr}}$ ) of 1.8–2.1 eV, respectively, between ions produced in the Colutron and the Nier source. Because we are dealing with threshold data, this difference should be caused by the maximum difference in the internal energy of the two projectiles. The maximum internal energy excitation of the  $\text{CH}_4^+$  from electron impact ionization in the Nier-type source was estimated (see above as 1.8 eV) and assuming no internal energy for the ions from the Colutron source there is semi-quantitative agreement with the above derived difference of 1.8–2.1 eV.

In conclusion, the data are again consistent with the assumption that the Colutron produced  $\text{CH}_4^+$  is practically completely relaxed as far as its internal energy is concerned, while the Nier-type source  $\text{CH}_4^+$  contains a substantial internal energy of up to a maximum value of 1.8 eV which is fully effective as additional energy to the internal energy acquired in the surface excitation in the subsequent dissociation processes.

### Acknowledgements

This work has been carried out within the Association EURATOM-ÖAW and in cooperation with the Association EURATOM-IPP.CR. The content of the publication is the sole responsibility of the authors and does not necessarily represent the views of the EU Commission or its services. Partial support of this work by FWF, ÖNB and ÖAW Wien, Austria, by the European Community, Brussels, and by the Grant Agency of the Czech Republic (Grant No. 203/00/632) is gratefully acknowledged.

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