The role of the methyl ion in the fragmentation of CH$_4^{2+}$

R Flammini$^{1,3}$, M Satta$^2$, E Fainelli$^1$, G Alberti$^1$, F Maracci$^1$ and L Avaldi$^1$

$^1$CNR-IMIP, Istituto di Metodologie Inorganiche e dei Plasmi, Area della Ricerca di Roma 1, Via Salaria km 29.300 CP10 00016 Monterotondo Scalo (RM), Italy
$^2$CNR-ISC, Istituto dei Sistemi Complessi, Via dei Taurini 19, 00185 Roma, Italy
E-mail: roberto.flammini@imip.cnr.it

Abstract. The fragmentation of the CH$_4^{2+}$ dication, formed upon C1s inner shell ionization and the following Auger electron decay, has been studied by means of Auger electron–ion and Auger electron–ion–ion coincidence spectroscopies at three different kinetic energies of the Auger electron, which correspond to the three main configurations ($1t_2^{-2}$, $1t_2^{-1}2a_1^{-1}$ and $2a_1^{-2}$) of the dication. For each ion pair detected in coincidence with the Auger electron, the dynamics of the dissociation is discussed. The results show that the fragmentation process is stepwise and mainly occurs via the formation and dissociation of the CH$_3^+$ intermediate. The orientation of the methyl ion, induced by a dipole moment during the first step of the fragmentation, is suggested to play a key role. Moreover, the experiments together with ab initio CAS calculations of the equilibrium geometries of the methane dication and the methyl cation provide information on the structure of the intermediate methyl ion.

3 Author to whom any correspondence should be addressed.
1. Introduction

The understanding of the fragmentation of polyatomic molecules with their richness of potential energy surfaces (PESs) and possible reaction channels represents a challenge for both experimentalists and theoreticians alike. High-level calculations are needed to describe properly the initial, intermediate and final states and to account for the dynamics of the process in each of the open channels, while only sophisticated and selective coincidence experimental techniques allow one to completely reveal the correlation among the final products. A prototypical target for such a study is represented by CH$_4$. Several techniques have been employed to study the fragmentation of the methane molecule, which has attracted a lot of attention due to the tetrahedral structure of its ground state. In particular, the fragmentation has been induced by electrons [1]–[4], protons [5], atoms [6]–[8], synchrotron radiation [9]–[13] and lasers [14, 15].

The different fragmentation pathways following valence ionizations [9]–[12], core excitations below the C1s threshold [3, 11, 16] and core ionization [11, 13] have also been investigated. Several ion fragments have been identified and their cross sections as a function of the energy have been measured [17]. Electron–ion and ion–ion coincidence techniques have also been employed [11, 13] to better characterize the break-up process. As for the theoretical side, some efforts have been devoted to the determination of the appearance potentials of specific ionic fragments [9, 18], the energy dependence of the cross section for the different channels [19], the identification of the electronic structure and symmetry of the excited or ionized molecule and the modeling of the dissociation process [9, 18, 20].

Recently, Kukk et al [13] used the Auger electron–ion coincidence technique to study the dissociation of the methane molecule, following the core–hole production by synchrotron radiation. These authors interpreted the experimental results in the framework of two limiting cases: the electronic-state- and excess-energy-dependent fragmentations.

When a single electronic state is involved, the dissociation is driven by the population and the energy of that dication state (electronic-state dependent), while if two or more dication states are involved, the partial yields of the fragments will depend on the available excess energy (excess-energy dependent). They suggested a concerted fragmentation for the highly excited dication states, where the reaction is mostly excess energy driven; while a
stepwise fragmentation (secondary decay) is proposed for the low excited dication states, i.e. an electronic-state-dependent fragmentation.

Here we have used the Auger electron–ion–ion coincidence technique to investigate the state-selected fragmentation of CH$_4^{2+}$. The selection of the energy of the Auger electron allows the identification of the dication states responsible for the dissociation. Then, the time correlation among the time-of-flights (TOFs) of the fragments allows the dissociation mechanism to be elucidated [21]. We show that the spatial orientation of the reaction intermediate can affect the dissociation process considerably when it occurs rapidly. As a consequence, the analysis of the detected ions provides information on the structure of the reaction intermediate.

In order to discuss in detail the mechanisms leading to the fragmentation of a molecule a proper definition of the sequence of events occurring is needed. In the literature, different nomenclatures have been used for such a sequence. According to Eland [21], stepwise fragmentations are named either initial charge separation (ICS) or deferred charge separation (DCS) depending on whether the two positive charges of a dication split in the first or the second step of the reaction. A combination of the two mechanisms may occur in cascade dissociations [22]. Otherwise when the bonds are cleaved simultaneously the process is called ‘instantaneous explosion’. According to the nomenclature of Maul and Gericke [23], when all the fragments depart simultaneously, i.e. a full break-up occurs in one step, the process is named synchronous concerted fragmentation. When the fragmentation occurs in two steps the process is named asynchronous concerted fragmentation if the second step occurs in a time shorter than the rotational period of the molecule. On the other hand, when the elapsed time between the two events is such that no memory of the orientation of the intermediate state is preserved, then the process is named sequential fragmentation. In our opinion, both the nomenclatures are needed: while the nomenclature of Maul and Gericke [23] more precisely points to the time dynamics of the process, the one of Eland [21] is more effective in description of the mechanism of the dissociation.

2. Experimental

The vacuum chamber (base pressure $\leq 10^{-7}$ mbar) used for these experiments is equipped with two spectrometers: a Wiley–McLaren TOF mass spectrometer (TOF-MS) [24] for the detection of ions and a cylindrical mirror analyzer (CMA) placed in front of the TOF-MS for the detection of electrons. A dc extraction field of 120 V cm$^{-1}$ 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 $\mu$s).
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 \textit{a posteriori}. The current 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. More details of the experimental setup and the procedures for the data collection are described elsewhere \cite{27} and will not be repeated here.

3. Computational details

The molecular structures of the neutral ground state of the methane, the electronically excited states of the methane dication and of the methyl ion have been calculated by full optimization in redundant internal coordinates. The complete active space (CAS) level of theory has been applied using a rational function optimization methodology. Six electrons in the active space formed by eight valence and virtual orbitals have been considered for the methane, whereas six electrons have been put in seven active orbitals for the methyl ion species. The basis set employed was formed by the Slater-type STO-6G orbitals \cite{26} for the occupied orbitals, and added with a modified STO-5G orbital for the virtual orbital. In particular, we decreased by a factor of 10 the exponential parameters. Symmetry constraint was applied neither to the shape of the molecular structure nor to the nature of the electronic orbitals. The transition state (TS) molecular structures were located with the help of the synchronous transit-guided quasi-Newton (STQN) method.

4. Results: the Auger electron and Auger electron–ion spectra

In figure 1, a diagram of the electronic states involved in the experiment is shown. On the left side, the doubly ionized states populated via the Auger decay are shown. It should be noted that the resolution of our electron analyzer does not allow the first three \(1^1T_2, 1^3T_2\) and \(1^1A_1\) states to be isolated, while the energy separation of the \(1^1T_2\) and \(1^1A_1\) excited states is large enough to allow their independent study. The \(3^1T_1\) and \(3^3T_2\) triplet dication states are not considered here due to their very low probability of being populated in an Auger process \cite{28}. In table 1, all the relevant data on the electronic states of the methane dication and methyl ion used in this work are summarized.

The lowest dissociation limits of the pair \(\text{CH}_3^+/\text{H}^+\) are shown on the right side of figure 1, while in the center of the figure the likely TS energies at their equilibrium geometries have also been highlighted. The lower excited states of the dication correlate to a TS, while the excited states at about 50 eV do not correlate to any stable TS.

The Auger spectrum of the \(\text{CH}_4\) (figure 2(a)) is characterized by three main features centered at about 250, 238 and 231 eV \cite{29}. These are attributed to dication states with \(1t_2^{-2}, 1t_2^{-1}2a_1^{-1}\) and \(2a_1^{-2}\) main configurations \cite{18, 30, 31}, respectively. In an electron impact experiment, all the processes leading to inner shell excitation and ionization may occur. As an example, in the spectrum of figure 2(a) there is a shoulder at about 257 eV that is not observed in the Auger spectra following \(\text{C}_1\)s photoionization. This feature is due to the spectator transitions...
Figure 1. Energy levels of the vertically excited CH₄ dication (CH₄²⁺)*, of the geometry relaxed CH₂⁺, and CH⁺. The circles represent the regions of the crossings among the PESs. The subscript ‘eq’ stands for ‘equilibrium’, as the calculations have been performed at the equilibrium configuration. The arrows next to the Auger electron energies indicate the energy resolution of the CMA.

Table 1. Data on the electronic states of the CH₄²⁺ and CH⁺ ions. ‘Min. energy’ is the energy of the minimum of the PES. ‘Int. energy’ is the energy available to the CH₄²⁺ dication. $D_e$ is the dissociation energy of the dication states. Vertical excitation energy corresponds to the calculated energy required to doubly ionize the neutral CH₄ at its equilibrium configuration. DIP is the measured double ionization potential $DIP = I_p(C_{1s}) - E_A$. All the tabulated values are in eV.

| Auger energy | Ionic state | Min. energy | Int. energy | $D_e$ (CH⁺ + H⁺) | Vertical excitation energy | DIP |
|--------------|-------------|-------------|-------------|------------------|--------------------------|-----|
| 231          | $^1A_1$     | 30.8        | 62.4        | 60.1             |                          |     |
| 238          | $^1T_2$     | 23.2        | 54.8        | 53.1             |                          |     |
| 250          | $^1A_1$     | 38.5        | 42.4        | 41.1             |                          |     |
|               | $^3T_2$     | 9.9         | 48.3        |                  |                          |     |
|               | $^3T_2$     | 35.9        | 42.4        | 41.0             |                          |     |
|               | $^3T_1$     | 33.8        | 38.7        |                  |                          |     |
|               | $^1E$       | 31.1        | 39.7        |                  |                          |     |
| 384          | $^3A_2'$    | 38.4        | 39.7        |                  |                          |     |
| 316          | $^1E'$      | 31.6        | 39.7        |                  |                          |     |
| 307          | $^3E'$      | 30.7        |             |                  |                          |     |
| 265          | $^1A_1$     | 26.5        |             |                  |                          |     |

from Rydberg excited states leading to the $1t_2^{-2}3sa_1^+$ final states [31]. The energy of the dication states is related to the kinetic energy (KE) of the Auger electrons by the relationship $DIP = I_p(C_{1s}) - E_A$, where $DIP$ is the double ionization potential, $I_p$ the C$_{1s}$ ionization energy [30] and $E_A$ the KE of the Auger electron. The three coincidence Auger electron–ion spectra measured
Figure 2. (a) C1s Auger electron spectrum of CH₄ measured at 4 keV electron incident energy. The bars indicate the Auger energies where the Auger electron–ion and Auger electron–ion–ion coincidence experiments have been performed. (b) Auger electron–ion coincidence spectra recorded at 231, 238 and 250 eV electron KE.

at the energies of the Auger electron mentioned above are shown in figure 2(b). No peaks due to the CH₂⁺ dication are observed at any of the energies studied. This confirms that no CH₂⁺ stable state exists [6]. The H⁺ yield is almost constant, whereas H₂⁺ is observed at 250 and 238 eV. The C²⁺ ion is observed at all the Auger electron energies without significant variation of its relative intensity. The yield of the CHₙ⁺ (n = 0–3) ions displays more interesting behavior. As the KE of the Auger electron decreases, a progressive increase of the relative intensity of the lighter fragments (H⁺, C⁺ and CH⁺) occurs. That atomization increases as the excitation energy of the

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dication increases has been observed in several polyatomic molecules. In the case of methane, this is in agreement with the measurements of the partial ion yield as a function of the Auger electron KE, as reported by Kukk et al [13].

Some features in figure 2 are characterized by a double peak shape. This is due to the finite angular acceptance of the TOF spectrometer. The extraction voltage applied in the interaction zone does not succeed in bending all the trajectories of the kinetic ions toward the detector; for example, the fast ions emitted perpendicularly to the ion-TOF axis are not collected. The label f (b) in figure 2, stands for forward (backward), and refers to the ions emitted in a cone toward (opposite to) the detector. The lack of the full angular efficiency mainly concerns the H+ and H2+ ions, while heavier fragments are collected over the full solid angle.

5. Results: the Auger electron–ion–ion spectra

The Auger electron–ion–ion coincidence maps corresponding to the Auger electron energies of 231, 238 and 250 eV are shown in figures 3, 4 and 5, respectively. The arrival times of the heavier and lighter fragments are reported on the vertical and horizontal axes, respectively. The maps are shown in false colors, and beside each map the color scale is shown. The (T1, T2) pairs of arrival times of the two ions in these maps should result in features of different shapes (lozenges, parallelograms, etc [33]) provided the full energy and angular distributions of the two fragments are detected. In our case, due to the angular acceptance of the TOF spectrometer, the features of each ion pair reduce to two enlarged spots [22].

A Monte Carlo simulation of the fragmentation process in the realistic conditions of our measurements shows that the limited angular acceptance alters the shape of the features in the three-dimensional (3D) maps, but does not compromise the determination of the slope of the regression line, provided the process is not characterized by a strong anisotropy. No anisotropy in the angular distribution of the ion fragments is expected in the present case because the molecular symmetry in the ground state is Td and in this point group the electronic transitions are independent of the molecular orientation (as in CF4 [38]). Moreover, the exciting beam of electrons can induce no anisotropy because it is not polarized. Even in the case of synchronous fragmentation where the charged fragments can be ejected with a relative angle different from 180°, all the information is preserved because the first ion that is collected is always the lighter one and the second heavier ion is collected over the full solid angle.

The slopes have been extracted from the experimental data according to the mathematical procedure suggested in [32]. In two-body reactions the momentum conservation forces the slope to be −1, while in three-body reactions, it can assume almost any value [21]. The values of the slopes extracted from the maps for each ion pair are reported in figures 3–5 and summarized in table 2.

To extract the kinetic energy release (KER) associated with an ion pair, the map has been projected on the vertical (heavier fragments) as well as along the horizontal (lighter fragments) axes. At variance with the KE extracted from the Auger electron–ion spectra that result from all the processes producing that particular ion, these projections provide only the KE of the process leading to a specific ion pair. The KEs have been calculated using the full width at half maximum (FWHM) [24] of the projections and are listed in table 3. Although these values are the upper bounds of the kinetic energy distribution (KED), they give a good estimation of the energy released in the process [25].
Figure 3. Auger electron–ion–ion coincidence map measured at an Auger electron energy of 231 eV. Next to each coincidence pair the value of the associated slope is reported.

Figure 4. Auger electron–ion–ion coincidence map measured at an Auger electron energy of 238 eV.

5.1. One-step fragmentation

In this section, we discuss the possibility that the synchronous concerted fragmentation, i.e. the molecule dissociates in two charged and \( n \) (\( n = 0–3 \)) neutral fragments at the same time, is the mechanism leading to the formation of \( \text{CH}_3^+–\text{H}^+ \), \( \text{CH}_2^+–\text{H}_2^+ \), \( \text{CH}_2^+–\text{H}^+ \), \( \text{CH}^+–\text{H}^+ \) and \( \text{C}^+–\text{H}^+ \) pairs.
5.1.1. CH$_3^+$–H$^+$. The CH$_3^+$–H$^+$ pair is observed at 250 eV (figure 5) and to a lesser extent at 238 eV (figure 4) but not at 231 eV (figure 3), although energetically allowed. In this last case, it is likely that the CH$_3^+$ fragment is produced in an excited state (for example the $^1E'$) and therefore suffers a further dissociation due to its higher internal energy content.

The slopes of the CH$_3^+$ and H$^+$ pair at 238 and 250 eV both show a value of $-1$ as was expected from momentum conservation. The broadening of the features along the bisectrix is due to the velocity distribution of the target molecules in the gas jet operated at room temperature and to the time resolution of the TDC [21].

5.1.2. CH$_2^+$–H$^+$. As in the case of the CH$_3^+$–H$^+$ pair, also the CH$_2^+$–H$^+$ ion pair has been observed only at the Auger energies of 250 and 238 eV (figures 4 and 5). This is consistent with the observation of the Auger electron–ion spectra of figure 2(b). The features are aligned along a line with slope $-1$, due to the momentum conservation. The two spots of the feature due to the CH$_2^+$–H$^+$ pair are more elongated along the bisectrix with respect to those of the CH$_3^+$–H$^+$ pair. This is due to the higher collection efficiency of the heavier H$_2^+$ with respect to H$^+$. Our calculations show that the H$_2^+$ ion is formed due to the intramolecular $\alpha$-elimination mechanism, with a barrier of about 2 eV in the case of the dication ground state configuration (TS leading to the CH$_2^+$ and H$_2^+$ fragments). The rearrangement of the atoms leading to H$_2^+$ ion is known to occur during fragmentation as reported in the literature in a similar system (CH$_3$Cl [37]).
The absence of this pair at 231 eV electron KE is due to the high internal energy content (30.8 eV) of CH$_2^+$ ion in the $^1A_1$ state.

Kukk et al [13] state that the CH$_4^+$ → CH$_2^+$ + H$_2^+$ reaction correlates well with the population of the term $^1T_2$ of the $1T_2^{-2}$ configuration. This finding is confirmed by our measurements also at 238 eV, where the $^1T_2$ term results from the $(2a_1^{-1}, 1T_2^{-1})$ configuration.

### 5.1.3. CH$_2^+$–H$^+$–H and CH$^+$–H$^+$–2H

The relative intensity of the CH$_2^+$–H$^+$ pair at the different Auger energies appears to decrease with the KE of the Auger electron. This is because when the CH$_2^+$ ion is produced at lower Auger KE (i.e. more internal energy available for the system to dissociate) it may undergo a further fragmentation leading to lighter fragments as for the case of CH$_2^+$ discussed in the previous section.

The KE associated with the proton remains substantially constant within the associated uncertainty, whereas the KE associated with the CH$_2^+$ fragment decreases (table 3) moving from 231 to 250 eV. This behavior seems to be not compatible with the observation of Kukk et al [13] who predict that KE increases as the Auger energy increases in the range 232–236 eV and then decreases at 250 eV (table 3). This difference may be attributed to the higher selectivity of the Auger electron–ion–ion coincidence technique that selects a particular fragmentation pathway, while in [13] an integration over all the processes producing the CH$_2^+$ ion is performed.

The CH$_2^+$–H$^+$ ion pair has been observed at all three Auger energies, with slopes varying from −1 at 231 eV to −0.93 at 250 eV. In contrast to the case of the CH$_2^+$–H$^+$ dissociation, the KE analysis shows that both fragments increase their KE as the internal energy of the system increases. This behavior is in agreement with the results of [13].

The case of a synchronous three-body concerted fragmentation has been studied in the literature and the observed shapes in the 3D $(T_1, T_2)$ maps are ‘egg-like’ [33]. The presence of a neutral fragment changes the slope and broadens the shape of the features in the map. Indeed, if the momentum of the neutral is aligned along the direction of the detected two charged

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**Table 3.** Experimental KE of the different fragmentation processes extracted from the Auger electron–ion–ion coincidence maps. In the fourth column, the values of [13] are reported.

| $E$ (eV) | Species | KE ± ΔKE | KE [13] | Species | KE ± ΔKE |
|---------|---------|----------|---------|---------|----------|
| 250 eV  | CH$_3^+$ | 0.28 ± 0.06 | 4.06 ± 0.83 |
|         | CH$_2^+$ | 0.35 ± 0.07 | 0.5     |
|         | CH$^+$   | 0.27 ± 0.06 | 0.4     |
|         | C$^+$    | 0.29 ± 0.05 | 0.4     |
|         | CH$_2^+$ | 0.65 ± 0.09 | H$^+$   | 4.49 ± 0.62 |
| 238 eV  | CH$_3^+$ | 0.37 ± 0.07 | H$^+$   | 5.51 ± 0.98 |
|         | CH$_2^+$ | 0.46 ± 0.08 | 1.1     |
|         | CH$^+$   | 0.40 ± 0.07 | 0.8     |
|         | C$^+$    | 0.24 ± 0.07 | 0.4     |
|         | CH$_2^+$ | 0.82 ± 0.10 | H$^+$   | 5.68 ± 0.70 |
| 231 eV  | CH$_3^+$ | 0.66 ± 0.09 | H$^+$   | 5.51 ± 0.97 |
|         | CH$^+$   | 0.51 ± 0.08 | 0.85    |
|         | C$^+$    | 0.15 ± 0.05 | 0.2     |

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fragments, only the slope will change. If the neutral fragment is ejected perpendicularly (at right angles) to this direction, then a broadening of the features occurs. The most likely case is intermediate between the two extreme ones and therefore the features in the 3D map are rotated and enlarged [25]. The features of this shape in the 3D maps are preserved also in the case of experiments with low angular acceptance as shown in the simulations of Le Brun [25]. In our data, only a broadening along the axis of the heavier fragment is observed.

5.1.4. \( {\text{C}^+}+{\text{H}^-}+3\text{H} \). This case has been discussed in the literature [13] using a Coulomb explosion model [39]. This model assigns to each hydrogen atom an equal fractional charge, because the hydrogen atoms in the ground state of the molecule are in equivalent positions. The fragmentation occurs in two stages: at the beginning the C–H bonds start to stretch rapidly, then, once the charge localization distance is reached, the Coulomb repulsion between the carbon atom and one of the hydrogen atoms becomes the dominant interaction. During the first stage, the carbon atom remains at rest because of momentum conservation. Afterwards, once the Coulomb repulsion has been switched on, the carbon ion and the proton begin to repel each other, arriving at the detector with anticorrelated momenta. As a consequence, the slope of a 3D ion–ion coincidence feature would have had a value of \(-1\). The slopes associated with the \( {\text{C}^+}/\text{H}^+ \) pair range from \(-0.51 \) to \(-0.80 \) when the Auger electron energy varies from 231 to 250 eV. Therefore the experimental results exclude the synchronous concerted mechanism for the production of this ion pair.

5.2. Two-step fragmentation

In this section, the production of the \( {\text{CH}_n^+}+{\text{H}^-}+{\text{H}^-} \) pairs via a two-step fragmentation will be discussed.

In the case of many-body dissociation, it is not always possible to infer unambiguously the leading mechanism from the 3D maps. The analysis carried out by Eland and Treves-Brown [36] precisely determines the limits of the ion–ion coincidence technique. However, in the present case the shape of the observed features may help in this regard. Indeed, the shapes of the \( {\text{C}^+}/\text{H}^+ \), \( \text{CH}^+/	ext{H}^+ \) and \( \text{CH}_2^+/	ext{H}^+ \) ion pair spectra appear to be broadened along the vertical axis (i.e. along the axis of the heavier fragments). This is typical of a two-step reaction in which the undetected fragments (neutral H and/or \( \text{H}_2 \)) are released in the second step of the dissociation after the ICS and affect the final KE (and thus the arrival time \( T_2 \)) of the heavier fragment. In this case \( T_2 \) displays a larger variation as the neutral fragment can be released in all directions [21].

5.2.1. \( \text{CH}_2^+–{\text{H}}^+–\text{H}^- \). The mechanism suggested for this fragmentation is a charge separation (\( \text{CH}_2^+–{\text{H}}^+ \)) in the first step followed by the release of the hydrogen atom (\( \text{CH}_2^+ \rightarrow \text{CH}_2^-+\text{H} \)) as reported in the literature [5, 9]. According to the model proposed by Eland [21], the value of the slope for this process is \(-0.93 \) (\(-14/15 \approx -m_{\text{CH}_2}+/m_{\text{CH}_2} \)) in the case of a pure sequential reaction. All of the measured slopes are smaller than this value, although those obtained at 238 and 250 eV (see table 2) may be consistent within their uncertainty with the value calculated in this manner. At 231 eV, a definitely smaller value \((-1.30 \) is measured. This value is quite peculiar as it is smaller than \(-1 \) even when the error bars are included.

If the second dissociation step occurs shortly after the first step, momentum conservation implies a further acceleration/deceleration of \( \text{CH}_2^- \), depending on the direction of ejection of the H atom. Assuming the structure of the \( \text{CH}_4 \) molecule depicted in figure 6(d), if H is released
Figure 6. Geometrical structures of the dication CH$_4^{2+}$ (a), the cation CH$_3^+$ (b) and the transition structure corresponding to the proton loss from CH$_4^{2+}$ in its electronic ground state $^1E$ (c). In panel (d), the labels useful in the discussion of the dissociation processes are reported.

into the half-space $\alpha$ ($\beta$) the CH$_2^+$ is decelerated (accelerated) and the associated slope will be larger (smaller) than $-0.93$. The slopes for the CH$_2^+/H^+$ ion pair are all smaller than $-1$; hence the neutral H has to be ejected in the $\beta$ half-space.

This can be explained considering the geometric structure of the CH$_4^{2+}$ and CH$_3^+$ ions in the states involved in the process and the fact that an electric dipole moment may be induced during the CH$_3^+ \rightarrow$ CH$_2^+\text{-H}$ dissociation.

It should be noted that both of the lower excited states $^1E$ and $^1T_2$ of the dication correlate with the $^1A'_1$ state of the methyl ion (see figure 1): in particular, the $^1E$ state, through the transition structure shown in figure 6(c). On the other hand, the $^1A_1$ dication state correlates
with the $^1E'$ of the methyl ion. Thus, while the higher dication states populated at 238 and 231 eV together with the $^1A_1$ state populated at 250 eV correlate to the $^1E'$ state of the CH$_3^+$, the dication states populated at 250 eV correlate to the $^1A_1'$ one. Now, let us consider the transition structure (figure 6(c)) formed in the first dissociation step for the case of the $^1E$ electronic ground state of the CH$_4^{2+}$. In this electronic state, the dication structure is planar. As the proton leaves CH$_4^{2+}$, the relative angle between the remaining C–H bonds increases from 90° to 120° (see the bottom panels of figures 6(a) and (c)).

In the dication ground state, an electric field exists along the H$^+$–CH$_3^+$ direction. During the second step of the dissociation, when a hydrogen atom departs, a dipole moment appears in the methyl ion, due to the stretching of the C–H bond. The behavior of the dipole moment as a function of the distance between the CH$_3^+$ and H, for the two $^1A_1'$ and $^1E'$ electronic configurations of the methyl ion, is shown in figure 7. In particular, in the ground state configuration the electric dipole moment is zero at the equilibrium geometry, then reaches a minimum negative value at a C–H bond distance of about 1.8 Å (figure 7(b)). An inversion of the dipole moment then occurs at about 3.5 Å, reaching the final value of 0.9 D of CH$_3^+$ in its ground state. In the $^1E'$ first singlet excited state, the minimum value for the electric dipole is reached at 1.5 Å and then it vanishes without changing sign (see figure 7(a)). This dipole moment induces an orientation of the methyl ion in such a way that the extending C–H bond will be aligned along the first dissociation axis, i.e. the H$_2$C$^+$–H$^+$ axis. This is due to the fact that the methyl ion screens the charge of the proton with the C–H bond. The orientation of the methyl ion fragment is effective only if the dipole-induced orientation occurs in a time shorter than the thermal rotation period of the molecule ($\approx 0.1$ ns) and if the electric field is strong enough. If we consider a maximum distance H$_2$C$^+$–H$^+$ of 100 Å the time elapsed for the methyl ion to be aligned is in the picosecond range ($\Delta t \approx 5$ ps). Once the rotation of CH$_3^+$ has occurred and the CH bond is aligned along the H$_2$C$^+$–H$^+$ axis, the relation [21] for a linear reaction (H$_2$C$^+$–H$^+$) can be applied:

\[
\text{slope}^{\exp}(\text{CH}_3^+/\text{H}^+) = \left( \frac{U_2}{U_1} \right)^{1/2} \mu^{1/2} \frac{m_{\text{CH}_3}}{m_{\text{CH}_2}},
\]

where $\mu = \frac{m_{\text{CH}_3} m_{\text{CH}_2}}{m_{\text{CH}_3} m_{\text{CH}_2}}$. Here, $U_1 = (16/15) \times \text{KE}(\text{H}^+)$ and $U_2$ are the overall kinetic energies released in the first and the second step of the dissociation, respectively. Thus, from the experimental values of the slope and the KE, it is possible to extract the value for $U_2$ at each Auger electron energy.

5.2.2. CH$^+$–H$^+$–2H. In the case of the CH$^+$–H$^+$ ion pair the hypothesis of a DCS should not be discarded. If a pair of H atoms is released in the first step, leaving the CH$_2^{2+}$ in an excited state [9], the charge separation may take place in the second step, leading to a slope value of about −1. This value is consistent with the measured slopes, which vary from −1 to −0.93, but a DCS cannot explain the observed broadening of the features in the 3D maps. Broad time distributions are attributed to the long lifetime of the precursor (CH$_2^{2+}$) that has the time to rotate freely before the subsequent Coulomb repulsion (CH$^+$ + H$^+$) occurs [21]. This leads to broad distributions along both the axes. In our case, the broadening is observed only along the heavier fragment axis. This suggests an energy sharing between the observed heavy charged fragment and the undetected neutral fragments.

A secondary decay (CH$_4^{2+}$ → CH$_3^+$ + H$^+$ and CH$_3^+$ → CH$^+$ + H + H) might be consistent with the observed values of the slopes, because the simple mass ratio gives −0.87,
Figure 7. Electric dipole momenta of the $1E'$ and $1A_1'$ of the CH$_3^+$ as a function of the C–H dissociation coordinate. The arrows indicate the magnitude and direction of the electric dipole moments with respect to the molecular frame.

$(-13/15 = -m_{\text{CH}^+}/m_{\text{CH}_3^+})$. The mismatch between the measured and calculated slopes can again be ascribed to a momentum release aligned with the momentum of the intermediate methyl ion.

The experimental slopes range between $-0.93$ and $-1$; hence the two hydrogens are released in the $\beta$ semispace of figure 6(d) in order to accelerate the CH$^+$ ion. For the $1A_1'$ ground state configuration of the CH$_3^+$, the calculations show a transition structure in which two hydrogen atoms are in the $\beta$ semispace, because the relative angle between the C–H bonds is 120°. On the other hand, when CH$_3^+$ is formed in the $1E'$ state the relative angle between the C–H bonds is 102°. For the excited states of the dication, no TS exist; however, the vibrational effects can account for the localization of the C–H bonds on the $\beta$ semispace.

Using the same arguments as those of Hansen et al [37] for CH$_3$Cl, we have generalized the equations of [21] to CH$_4$, which is not a linear molecule but for the present purposes can be
Figure 8. $U_2$ as a function of the angle $\theta$ for the fragmentation processes studied at the three different Auger electron energies. The energy values of table 1 have been used to extract the extreme values for the parameters $\theta$ and $U_2$. The allowed values of $U_2$ and $\theta$ have been highlighted by the thicker line.

treated as a linear one. When the $^1A'_1$ cation state is considered, the two C–H bonds belong to the $\beta$ semispace and if a release of the two equivalent hydrogen atoms occurs simultaneously, the momentum conservation acts only along the first dissociation axis as the perpendicular components of the momenta of the two H atoms cancel out. Thus, using the experimental slope and the angle $\theta$ defined as the angle between the bond CH$^+$–H$^+$ and (the two equivalent) bonds CH$^+$–H, derived from the calculations, it is possible to give an estimation of $U_2$ using the following parametric equation derived in [37]:

$$
(cos \theta)^2 U_2 = \frac{U_1}{2\mu} \left[ \text{slope}^{\text{exp}}(\text{CH}^+/\text{H}^+) + \frac{m_{\text{CH}}}{m_{\text{CH}_3}} \right]^2,
$$

(2)

where $U_1$ and $\mu$ are defined as in equation (1). Equation (2) describes the behavior of the parameters $\theta$ and $U_2$. In the hypothesis that CH$^+$ is in its ground state, it is possible to infer the upper limit of the KE released in the second dissociative step. Indeed $U_2 \leq E_{\text{int}} - U_1$, where $U_1$ is the KE released in the first step and $E_{\text{int}}$ the energy available for the system at each Auger electron energy (table 1). The function $U_2 = U_2(\theta)$ is strictly monotonic above 90° (see figure 8) and thus a single valued function. Using these upper values for $U_2$, we can calculate the corresponding $\theta$ angles at each Auger energy. Conversely, $\theta$ cannot exceed the values of 102° or 120° at equilibrium geometry, depending on the CH$^+_3$ state considered. Using these $\theta$ values, the lowest values of $U_2$ can be estimated. The results, summarized in table 4, show that if all the energy available is converted into KE, the two hydrogen atoms are emitted perpendicularly to the first dissociation axis. This can be rationalized in the case of the lowest dication state ($^1E$): when the content of internal energy is large in the methyl ion, the two hydrogen atoms are released promptly after the proton departure (at about 90°). Otherwise the methyl ion reaches its equilibrium structure due to the charge repulsion and then releases the two hydrogens at 120° with lower KE (figure 8).

In contrast to the CH$^+_3$–H$^+$ case, the dipole moment plays no role here, due to a geometrical reason: when the two C–H bonds begin to stretch and the dipole moment switches on, no orientation of the methyl ion occurs because the dipole moment is already aligned along the H$_3$C$^+$–H$^+$ electric field.

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Table 4. Range of the $U_2$ and $\theta$ values for the processes leading to the different ion pairs at the three measured energies (see text).

| Ion pair     | Auger energy (eV) | $U_1$ (eV) | Slope     | $U_2$ (eV) | $\theta$ (deg) |
|--------------|-------------------|------------|-----------|------------|----------------|
| $C^+/H^+$    | 231               | 7.66       | $-0.51$   | 10.0↔23.1  | 70↔77         |
|              | 238               | 6.76       | $-0.68$   | 2.9 ↔ 16.4 | 70 ↔ 82       |
|              | 250               | 5.88       | $-0.80$   | 0          |                |
| $\text{CH}^+/H^+$ | 231          | 7.10       | $-1$      | 23.1 ↔ 0.74 | 92 ↔ 102       |
|              | 238               | 5.88       | $-0.98$   | 17.2 ↔ 0.44 | 92 ↔ 102       |
|              | 250               | 4.33       | $-0.93$   | 4.3 ↔ 0.018 | 92 ↔ 120       |
| $\text{CH}_2^+/H^+$ | 231          | 5.87       | $-1.30$   | 0.16        |                |
|              | 238               | 5.87       | $-1.09$   | 0.00094     |                |
|              | 250               | 4.33       | $-1.11$   | 0.0037      |                |

5.2.3. $C^+-H^+-3H$. As for this process, considerations about the symmetry of the valence orbitals led Kukk et al [13] to suggest a secondary decay process at 238 and 250 eV, and a simultaneous fragmentation at 231 eV, where the $2a_1^{-2}$ configuration has the same tetrahedral symmetry as the neutral molecule and the remaining electronic charge is still equally distributed. On the other hand, when the $1t_2^{-1}$ orbital is involved, the expected asymmetry in the electronic charge makes a secondary decay more likely. In the section devoted to the one-step fragmentations, we discarded the possibility of a simultaneous process, due to the values of the slopes far from $-1$. For the same reason the DCS can be ruled out.

If we assume that the fragmentation process is sequential and the two stages are well separated in time, the model suggests a slope of $-0.8$ ($m_{C}/m_{\text{CH}_3} = -12/15$) [21]. This value is in perfect agreement with the slope measured at 250 eV.

A step forward can be made in the interpretation of the values measured at 231 and 238 eV Auger electron energies considering the case of a linear reaction [21]. Indeed, when a two-step dissociation occurs and the energy $U_2$ released in the second step is not vanishing, the model predicts a correction to the slope which is related to the ratio between the energies released in the two steps and the masses of the fragments involved [21]. This is expected to occur if the momentum released in the second step is aligned along the axis of the first step of the dissociation. The neutral release must take place on a timescale shorter than that of the rotation of the intermediate ($\sim 0.1$ ns) [21].

Now the question is whether the $\text{CH}_2^+ \rightarrow C^+ + H^+ + 3H$ dissociation can be considered a linear reaction. As outlined by Hansen et al [37], it is not necessary to have a linear molecule to consider a linear reaction, but only that the momenta of all the species released in the second step result in a total momentum aligned only along the first dissociation axis. This is expected to occur if the $\text{CH}_2^+$ fragment is still in its pyramidal form. In the case of the methane molecule, the fragmentation $\text{CH}_3^+\rightarrow\text{H}^+$ identifies the first dissociation axis. Then, if the subsequent dissociation is fast enough, i.e. the dissociation occurs without relaxation into the equilibrium geometry, the $\text{CH}_2^+$ remains in its pyramidal configuration, with the top of the pyramid (the carbon atom) oriented toward the ejected proton. This means that the momenta of the three hydrogen atoms (just before their release) are directed along the edges of the triangular pyramid, from the vertex to the base. The projections of these three momenta on the base of the pyramid cancel out due to the triangular symmetry. Therefore only the sum of the projections of the three momenta along
the first dissociation axis survive. If the three hydrogen atoms are released at the same time, the momentum conservation will cause a net contribution with opposite sign to the momentum of the C$^+$ ion, which, as a consequence, will be slowed down. Then the reduced time separation between the C$^+$ ions emitted in the backward and forward directions as the binding energy increases can be ascribed to the effect of the release of the three hydrogen atoms. The larger the energy available for the dissociation, the larger is the energy released in the second step and the smaller is the splitting in the flight time of the C$^+$ ions. This reduces the slope of the C$^+$–H$^+$ ion pair.

The assumption of the pyramidal configuration of the CH$_3^+$ and the concurrent release of the three hydrogen atoms can be justified as follows. The neutral CH$_4$ molecule is a tetrahedron, belonging to the $T_d$ group. When it is doubly ionized following the Auger decay, the molecule is still in the tetrahedral geometry [18, 29]. The axis along which the ICS occurs (CH$_3^+$–H$^+$) is the C$_3$ symmetry axis for the three C–H bonds of the CH$_3^+$ fragment. Although the literature reports that the CH$_3^+$ ion in the lowest excited states is a planar molecule ($\in D_{3h}$ group), the deformation of the methyl ion from the tetrahedral configuration of the dication to the planar geometry of the CH$_3^+$ does need to pass through the pyramidal configuration ($\in C_{3v}$). This has already been proposed for the CH$_3$Cl fragmentation by Liu et al [40]. In our case, a fast second dissociation step is compatible with the excited states of the dication populated at 238 and 231 eV which rapidly dissociate. In the literature [5], CH$_4$ is known to undergo a rapid dissociation and similar sp$_3$ hybridized molecules have already shown evidence of fast dissociation (CD$_4$ [11], CF$_4$ [41] or CH$_3$Cl [37]). This supports our assumption.

Now, within the framework of the above hypothesis, we can use the generalization of the equations of [21] proposed by Hansen et al [37] for the CH$_3$Cl molecule:

$$ (\cos \theta)^2 U_2 = \frac{U_1}{3^2 \mu} \left[ \text{slope}^{\exp}(\text{C}^+/\text{H}^+) + \frac{m_C}{m_{\text{CH}_3}} \right]^2. \quad (3) $$

In this formula, $\theta$ is the angle between the CH$_3^+$–H$^+$ and C$^+$–H dissociation axes. In our case, the three possible axes of the second dissociation are equivalent with respect to the first dissociation axis. The factor 3 in the denominator of equation (3) accounts for the sum over the three components. As for equation (2), we can treat $U_2$ and $\theta$ as the parameters of a parametric equation. In figure 8, $U_2$ is plotted as a function of $\theta$.

The minimum values for the angle $\theta$ can be estimated. If the second step of the dissociation is so fast that at the moment of release of the three hydrogen atoms the methyl ion is still in its pyramidal structure (simply a $T_d$ structure without a CH bond), then $\theta$ is equal to 70$^\circ$. At 238 and 231 eV Auger electron energy, the states populated are immediately dissociative and $U_2$ is equal to 2.9 and 9.9 eV, respectively. These values are consistent with the available energy for the system to dissociate (table 1).

On the other hand, if the values of the internal energies reported in table 1 are used, it is possible to extract the maximum values for $\theta$. Upper limits of 77$^\circ$ and 81.7$^\circ$ at 231 and 238 eV, respectively (figure 8), can be derived. Thus if all the energy available to the dissociating system is transferred to the second dissociation step, the CH$_3$ is in its pyramidal configuration.

In contrast to what happens in the case of the CH$^+/\text{H}^+$ coincidence pair, the hydrogen atoms are released in the $\alpha$ semispace, decelerating the C$^+$ ion. That is the reason why the functional dependence $U_2(\theta)$ is reversed with respect to the CH$^+$ ion, which is, in contrast, accelerated by the release of the neutrals.
Once provided with the alignment between the two steps of the fragmentation, the behavior of the energy released in the second step suggests that in the case of the CH$_2^+$/H$^+$ pair, the $U_2$ plays almost no role (and the process is essentially sequential), whereas in the case of the C$^+$/H$^+$ pair it does. Indeed, the values of $U_2$ are never negligible with respect to $U_1$ (except at 250 eV).

The behavior of the CH$^+$/H$^+$ pair is intermediate between the CH$_2^+$/H$^+$ and C$^+$/H$^+$ cases: while the lower limits of $U_2$ allow, to some extent, the interpretation in terms of a sequential decay, in general this is not possible and the alignment of the momenta must not be neglected (asynchronous decay).

It should be noted that while small differences have been observed between the values of $U_1$ at the three energies measured and in the different fragmentation processes, large variations are associated with $U_2$, depending on the number of bonds cleaved in the second step of the dissociation. At lower Auger electron energies, when the internal energy is large, the system still prefers to dissociate in two steps, transferring to the second step most of its available energy.

6. Conclusions

A study of the fragmentation of the methane molecule is reported. First, an inner shell (C 1s) ionization is produced by electron impact, then via the Auger electron decay the CH$_2^+$ dication is produced. The CH$_2^+$ breaks up following several different fragmentation pathways. The Auger electron–ion and Auger electron–ion–ion coincidence spectroscopies complemented by ab initio CAS calculations made us understand how the dication states correlate with each fragmentation channel.

As far as the one-step processes are concerned, Coulomb explosion of CH$_2^+$/H$^+$ and CH$_3^+$/H$^+$ have been reported. The production of the H$^+_2$ ion has been attributed to the intramolecular $\alpha$-elimination. Two-step processes have been identified as the main mechanism leading to CH$_n^+$/H$^+$ ($n = 0$–2) pairs. The production of these ion pairs has been ascribed either to a sequential decay or to an asynchronous concerted reaction, after ICS. These findings are consistent with the proton impact fragmentation studies of [5]. The shape and slopes associated with the features of these ion pairs in the 3D maps ruled out the possibility of synchronous concerted reactions. All of the two-step processes have been described as linear reactions generalizing the equations developed in [37]. In the case of the CH$_2^+$/H$^+$ ion pair, the importance of the dipole-induced orientation of the intermediate methyl ion has been demonstrated. As far as the CH$^+$/H$^+$ ion pair is concerned, the alignment of the methyl ion with respect to the first dissociation axis suggested a release of the two hydrogen atoms in the same plane as the initially ejected proton. A special case is the atomization of the CH$_3^+$ dication leading to the C$^+$, H$^+$ and three H fragments, which has also been successfully described as a two-step process. The specific values of the ion TOFs of the C$^+$/H$^+$ coincidence pair have been interpreted again as due to the alignment of the momenta of the fragments between the first and the second step of dissociation. Moreover, considerations about the spatial symmetry of the intermediate CH$_3^+$ fragment ion in the hypothesis of an ‘asynchronous concerted’ decay process have led us to disentangle the most likely structure of the methyl ion, just before the second step of the dissociation. Indeed, our results indicate that in the first excited electronic states of CH$_3^+$, the three hydrogen atoms are released while the methyl ion is still in a pyramidal structure.

To our knowledge, this is the first example where electron–ion–ion coincidence experiments provide information on the structure of the intermediate ion in a stepwise fragmentation.

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