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Reactions of State-Selected Atomic Oxygen Ions

$O^+(^4S, ^2D, ^2P)$ with Methane

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ABSTRACT

An experimental study has been carried out on the reactions of state selected $O^+(^4S, ^2D, ^2P)$ ions with methane with the aims of characterizing the effects of both the parent ion internal energy and collision energy on the reaction dynamics and determining the fate of oxygen species in complex media, in particular the Titan ionosphere. Absolute cross sections and product velocity distributions have been determined for the reactions of $^{16}O^+$ or $^{18}O^+$ ions with CH_4 or CD_4 from thermal to 5 eV collision energies by using the guided ion beam (GIB) technique. Dissociative photoionization of O_2 with vacuum ultra-violet (VUV) synchrotron radiation delivered by the DESIRS beamline at the SOLEIL storage ring and the threshold photoion photoelectron coincidence (TPEPICO) technique are used for the preparation of purely state-selected $O^+(^4S, ^2D, ^2P)$ ions. A complete inversion of the product branching ratio between CH_4^+ and CH_3^+ ions in favour of the latter is observed for excitation of O^+ ions from the 4S ground state to either the 2D or the 2P metastable state. CH_4^+ and CH_3^+ ions, which are by far the major products for the reaction of ground state and excited states, are strongly backward scattered in the center of mass frame relative to O^+ parent ions. For the reaction of $O^+(^4S)$, CH_3^+ production also rises with increasing collision energy but with much less efficiency than with O^+ excitation. We found that a mechanism of dissociative charge transfer, mediated by an initial charge transfer step, can account very well for all the observations, indicating that CH_3^+ production is associated with the formation of H and O atoms ($CH_3^+ + H + O$) rather than with OH formation by an hydride transfer process ($CH_3^+ + OH$). Therefore, as the CH_4^+ production by charge transfer is also associated with O atoms, the fate of oxygen species in these reactions is essentially the O production, except for the reaction of $O^+(^4S)$, which also produces appreciable amounts of H_2O^+

ions, but only at very low collision energy. The production of O atoms and the nature of the states in which they are formed are discussed for the reactions of O^+ ions with CH_4 and N_2 .

INTRODUCTION

For a good understanding of the reaction dynamics of a system, it is important to carry out experimental studies for which as much as possible initial and final parameters are controlled. In this work, we want to shed some light on the $O^+ + CH_4$ reactive system by controlling both the electronic energy of the O^+ reactant and the collision energy and by characterizing the reaction cross sections and the product velocity distributions as a function of the initial conditions.

Reactions of atomic O^+ ions are important in various complex environments such as planetary ionospheres or plasmas. The importance of the $O^+(^2D, ^2P)$ metastable states have been stressed for a long time for instance for Earth¹⁻⁴ and Venus⁵ atmospheres. As their lifetimes are very long, 1.6 and 9.1 h for $^2D_{3/2}$ and $^2D_{5/2}$, and 6.3 and 4.9 s for $^2P_{1/2}$ and $^2P_{3/2}$ respectively,⁶ these metastable species have time to react before their deexcitation, and as they carry 3.3 and 5 eV of electronic energy, their reactivity is expected to be different from that of the ground state. Three oxygen-bearing molecules have been observed in Titan's atmosphere so far (CO , CO_2 , and H_2O). Their sources are one of the keys to further our understanding on the atmosphere's origin, evolution and molecular complexity but they are still under debate. Their presence was first attributed to an internal source of CO or by assuming that CO is the remnant of a larger primordial abundance, in addition to an external source of H_2O from micrometeorite ablation but none of these processes could simultaneously reproduce the observed abundances of all three species.⁷ After the *Cassini* spacecraft detected the presence in the Saturn system of some energetic O^+ originating from the gushing geysers of Enceladus,⁸ a modeling study showed that

these ions could be at the origin of the abundance of oxygen-bearing species in Titan's atmosphere.⁹ However, this model over predicts two recent measurements (from *Cassini* and *Herschel*) that provided stronger constraints on the H₂O abundance in Titan's atmosphere.¹⁰⁻¹¹ Finally, since the lifetimes in Titan's atmosphere of H₂O, CO₂ and CO are significantly different (~ 10 yr, ~ 500 yr and ~ 1 Gyr, respectively), a time-variable external source, involving a decrease in the OH/H₂O flux over the last centuries, has been put forward to explain the observed profiles.¹² One of the major uncertainties in these scenarios is the fate of the O⁺ ions upon impact in the Titan's upper atmosphere. Therefore, it appears very important to characterize the reactions of O⁺ with the most abundant neutral molecules of Titan's atmosphere, N₂ and CH₄, and in particular determine the nature of the oxygen product formed (O(³P), O(¹D), OH, H₂O).¹³

The reactions of O⁺(⁴S, ²D, ²P) with N₂ have been well characterized experimentally as a function of the temperature and collision energy.^{3, 14-32} The reaction of ground state O⁺(⁴S) ions mainly leads to NO⁺ + N, whereas charge transfer leading to N₂⁺ + O products is greatly enhanced in the reaction of the metastable O⁺(²D, ²P) ion on a large collision energy range, as reviewed by Lindsay and Stebbings.³¹ The importance to consider the reactions with methane stems from the multiple other possible oxygen bearing products, such as H_xO⁽⁺⁾ (with x = 1-3) or H_yCO⁽⁺⁾ (with y = 0-3), which could initiate a very different chemistry. Many product reaction channels among the (O1-O10) processes listed below have been identified and discussed in experimental³³⁻³⁸ and theoretical³⁸⁻⁴⁰ studies of the reaction of atomic oxygen ions with methane:

Figure 1. Energy diagram for the $\text{O}^+(\text{}^4\text{S}, \text{}^2\text{D}, \text{}^2\text{P}) + \text{CH}_4$ reaction.

The energetics in equation (O1-O10) are given for ground-state reactants and products and for the most abundant isotopes, ^{16}O and $^{12}\text{CH}_4$. These channels are displayed in Figure 1 together with channels, which will be discussed later, where reactants or products are in electronically excited states. Note that small shifts in energy exist when other isotopes, ^{18}O or CD_4 , are used due to differences in zero point energies. For instance, using the most accurate values of the ionization potential of O ($13.61806 \pm 0.00008 \text{ eV}$)⁴¹, CH_4 and CD_4 (12.618 ± 0.004 and $12.672 \pm 0.003 \text{ eV}$ resp.)⁴² and the appearance energies for $\text{CH}_4 \rightarrow \text{CH}_3^+ + \text{H}$ ($14.323 \pm 0.001 \text{ eV}$)⁴³ and $\text{CD}_4 \rightarrow \text{CD}_3^+ + \text{D}$ ($14.4184 \pm 0.001 \text{ eV}$)⁴⁴, the ΔH value varies from -1.000 to -0.946 eV for (O1) and from 0.705 to 0.800 eV for (O3) which represent differences lower than 0.1 eV.

The rate constant of the $\text{O}^+(\text{}^4\text{S})$ reaction at 300 K has been determined in selected ion flow tube (SIFT) experiments by Smith et al,^{33, 36} in conditions where the metastable states are quenched, and was found to be very fast, 1.0 and $1.1 \cdot 10^{-9} \text{ cm}^3 \cdot \text{s}^{-1}$, and very close from the Langevin capture rate ($1.3 \cdot 10^{-9} \text{ cm}^3 \cdot \text{s}^{-1}$). The only products identified in these experiments are CH_4^+ and CH_3^+ in a ratio between $0.89 : 0.11$ ³³ and $0.80 : 0.20$ ³⁶. Studies of near thermal to 15-20 eV collisions of $\text{O}^+(\text{}^4\text{S})$ with CH_4 and CD_4 ,³⁸ and larger hydrocarbons, $\text{C}_n\text{H}_{2n+2}$ ($n=2-4$),⁴⁵ have been conducted by Levandier et al, in order to understand the effects of the exposure of spacecrafts to low orbit environment during the reentry in Earth atmosphere. In these experiments, using the GIB technique,⁴⁶ metastable O^+ species were maintained below 1% by using dissociative ionization of CO_2 with electrons of approximately 20 eV to produce the O^+ ions.³⁸ In addition to CH_4^+ (the main product) and CH_3^+ ions, a large number of other products of the $\text{O}^+(\text{}^4\text{S})$ reaction with methane formed by the (O1-O10) processes, including H_xCO^+ products for which a new C-O bond is formed, have been observed with high sensitivity. Absolute reaction cross sections and product velocity distributions have been measured and discussed in great detail with the help of

ab-initio electronic structure calculations in the study.³⁸ This study will thus serve as a reference in the present work for the comparison of ground and metastable states reactivity. Note also that these results³⁸ have been reanalyzed soon after their publication with the help of classical trajectory simulations³⁹ on the ground state quartet surface for collision energies ranging from 0.5 to 10 eV using the PM3 hamiltonian with special emphasis on the products different from the main CH_4^+ one.

To our knowledge, the only experimental studies reported in the literature on the reactivity of metastable O^+ ions with methane are the experiments by Kusunoki et al³⁴ and Ottinger et al³⁵ in which almost pure $\text{O}^+(\text{}^4\text{S})$ or mixed $\text{O}^+(\text{}^4\text{S}, \text{}^2\text{D}, \text{}^2\text{P})$ population with a proportion of about 30-35 % metastable species³⁵ are produced from CO gas in a plasma ion source by changing the pressure and the ion-source voltage. In the first study,³⁴ chemiluminescence was observed in the reaction of O^+ with CH_4 , C_2H_4 , C_2H_6 and C_3H_8 target at a relatively high reaction cell pressure of 10^{-2} Torr and identified to OH emission mainly. For the CH_4 case, clear evidence of second order reactions was found.³⁴ In the second study,³⁵ a combined electric and magnetic sector mass spectrometer was used to record OH^+ , CH_3^+ and CH_4^+ primary production and CH_5^+ secondary production in the $\text{O}^+ + \text{CH}_4$ reaction at collision energies between 2 and 15 eV and for target gas pressures between $2 \cdot 10^{-4}$ and 10^{-2} Torr. Reaction cross sections were derived from the extrapolation at the lowest pressures showing the increase of CH_3^+ production for the reactivity of the metastable states.³⁵ A very recent theoretical work by Hrušák et al,⁴⁰ using the MCSCF approach has considered the lowest 19 states of A' symmetry to encompass the energy window including the $\text{O}^+(\text{}^4\text{S}, \text{}^2\text{D}, \text{}^2\text{P})$ entrance channels and demonstrating the difficulty of the task to treat the dynamics on a 10 eV energy range. For the moment, the study is focused on the $\text{O} + \text{CH}_4^+$, $\text{OH} + \text{CH}_3^+$ and $\text{OH}^+ + \text{CH}_3$ product channels only and the PES is calculated along a

“chemically reasonable intuitive reaction coordinate” (CRIRC). Further calculations are planned in the future to provide a more complete set of PES calculations that will be helpful to discuss all the other important channels, in particular the dissociative charge transfer channel, $\text{CH}_3^+ + \text{H} + \text{O}$.

To prepare purely state-selected $\text{O}^+(\text{}^4\text{S}, \text{}^2\text{D}, \text{}^2\text{P})$ ions, two methods have been used so far. In the group of C. Ng,^{27, 47-48} the dissociative charge transfer of Ar^+ , Ne^+ and He^+ rare gas cations on O_2 is used to produce $\text{O}^+(\text{}^4\text{S})$, $\text{O}^+(\text{}^2\text{D})$, and $\text{O}^+(\text{}^2\text{P})$ ions respectively and study state-selected reactions,^{27, 49} in particular the reaction of $\text{O}^+(\text{}^4\text{S}, \text{}^2\text{D}, \text{}^2\text{P})$ with N_2 .²⁷ Dissociative photoionization of O_2 associated with the TPEPICO technique⁵⁰⁻⁵¹ can also be used to produce state-selected $\text{O}^+(\text{}^4\text{S})$, $\text{O}^+(\text{}^2\text{D})$, and $\text{O}^+(\text{}^2\text{P})$ ions with photon energies between 18.7 and 24 eV, because these states are known to be efficiently produced in coincidence with threshold electrons.⁵²⁻⁵⁵ This technique has already been used to study the reactivity of state-selected O^+ ions with N_2 ²⁴ and CO_2 .⁵⁶

Following the latter method, we are reporting here on the study of the reactions of purely state-selected $\text{O}^+(\text{}^4\text{S}, \text{}^2\text{D}, \text{}^2\text{P})$ with methane at collision energies ranging from thermal energies, where many reactive channels including formations of new C-O bonds have been observed for the reaction of the ground state, to higher energies (several eV) where usually only more direct processes, such as charge, H, H^- or H^+ transfer, are possible. To avoid mass overlaps between parent and/or product ions present in the $^{16}\text{O}^+ + \text{CH}_4$ system, it was necessary to work on the isotopically substituted systems, $^{16}\text{O}^+ + \text{CD}_4$ and $^{18}\text{O}^+ + \text{CH}_4$. The objectives of the presented study are twofold: i. the characterization of the reaction dynamics, by comparing in particular the effect of O^+ parent ion internal energy and collision energy on the reactivity and ii. To provide data to modelers for a better understanding of the chemistry of complex media, such as planetary

ionospheres, with a special interest for the characterization of the nature of oxygen bearing products in relation with the problem of the oxygen chemistry on Titan.

EXPERIMENTAL METHODS

The experimental setup used in this work, called CERISES (Collision et Réactions d'Ions Sélectionnés par Electrons de Seuil), has been extensively described in a previous study⁵⁶, already concerning the reactivity of state-selected atomic ions, namely $N^+(^3P, ^1D)$ and $O^+(^4S, ^2D, ^2P)$, which was done with vacuum-ultraviolet (VUV) synchrotron radiation (SR) from the Super-ACO storage ring at LURE, the former French synchrotron laboratory. In this work, the VUV radiation used is provided by the DESIRS beamline⁵⁷ at the French 2.75 GeV storage ring SOLEIL. Thus, only the main experimental points and the particularities associated with the new SR source will be emphasized in this section.

Generalities

Figure 2. Schematics of the CERISES experimental setup. QI and QII : 1st and 2nd quadrupole mass filters; OI and OII : 1st and 2nd octopole RF guides.

CERISES is an apparatus devoted to ion-molecule reaction studies using the guided ion beam (GIB) technique.⁴⁶ It is based on the association of four radio-frequency (RF) devices, a first

quadrupole mass filter (QI), a first octopole guide (OI) terminated by a 4 cm long reaction cell, a second octopole guide (OII) and a second quadrupole mass filter (QII) as sketched in Figure 2.

The $^{16}\text{O}^+$ and $^{18}\text{O}^+$ parent ions are produced in the source by dissociative photoionization of $^{16}\text{O}_2$ and $^{18}\text{O}_2$ (97% ^{18}O atom enriched from Euriso-Top) molecules with VUV radiation in the 18.7 - 24 eV photon energy range and state-selected as detailed in the following sub-section. The photons are delivered by the undulator-based beamline DESIRS⁵⁷ equipped with a 400 lines/mm grating optimized for the high energy range of the beamline. After their extraction from the source, the parent ions are mass selected by the 1st quadrupole QI before being injected in the 1st octopole OI. The reaction takes place with the methane thermal (300 K) neutral target, either CH_4 or CD_4 (99% D atom enriched from Euriso-Top), in a reaction cell constituted by a cylinder covering the last 4 cm of OI. The absolute pressure of the neutral target monitored by a Baratron type gauge is maintained at a value close to 10^{-4} Torr, a compromise between sensitivity and limitation of secondary reactions that cannot be completely avoided for this system as shown below. Parent and product ions are then extracted into the 2nd octopole OII by a small voltage (0.7 V) between the two octopoles to avoid trapping of slow product ions and their subsequent reactions, mass analyzed in the 2nd quadrupole QII and finally detected by a multichannel plate detector.

From the parent and product ion signals and the methane pressure measurement, absolute reaction cross sections can be derived after calibration of the effective length of the reaction cell done using the well determined cross section of the $\text{Ar}^+ + \text{D}_2 \rightarrow \text{ArD}^+ + \text{D}$ reaction.⁵⁸

Attenuation of the parent ion beam and contribution of reactions that occur in the octopoles outside the reaction cell are taken into account by recording the ion signal while sending the target gas either into the cell or directly into the octopole chamber.

The translational energy, E_{LAB} , of the O^+ parent ions in OI and hence the collision energy, can be varied from thermal energies up to 20 eV by changing the potential of OI relative to the potential of the source where the O^+ ions are created. The effective value of E_{LAB} and its width (≈ 0.3 eV FWHM) are measured in OI by a retarding potential method. In our configuration, the main sources of broadening are the finite size of the ion creation zone and the effect of the transmission of the ions through the first quadrupole. In principle, E_{LAB} also depends on the initial energy of the parent ion in the source that could be important in dissociative ionization. However, this is negligible here for the state-selected experiments as, exclusively O^+ ions that are formed exactly at the thresholds for dissociative ionization, i.e. without recoil energy, are used in these experiments, as explained in the following sub-section. The mean value of the collision energy in the center of mass (CM) frame, E_{CM} , is the product of E_{LAB} by the factor $m_2 / (m_1 + m_2)$ where m_1 and m_2 are the m/z values for the O^+ parent ion and the methane target gas, respectively. This mass factor, slightly changing with isotope substitutions, is close to $\frac{1}{2}$ here, allowing for E_{CM} values up to 10 eV with a width (FWHM) of about 0.15 eV.

Production of state-selected $\text{O}^+(\text{}^4\text{S}, \text{}^2\text{D}, \text{}^2\text{P})$ ions

#	O^+ and O states	E (eV)
1	$\text{O}^+(\text{}^4\text{S}) + \text{O}(\text{}^3\text{P})$	18.73
2	$\text{O}^+(\text{}^4\text{S}) + \text{O}(\text{}^1\text{D})$	20.70
3	$\text{O}^+(\text{}^2\text{D}) + \text{O}(\text{}^3\text{P})$	22.06
4	$\text{O}^+(\text{}^4\text{S}) + \text{O}(\text{}^1\text{S})$	22.92
5	$\text{O}^+(\text{}^2\text{P}) + \text{O}(\text{}^3\text{P})$	23.75
6	$\text{O}^+(\text{}^2\text{D}) + \text{O}(\text{}^1\text{D})$	24.03

Table 1. Energies (in eV) of O₂ dissociative ionization limits relative to the ground state of the neutral O₂ molecule.

O⁺ ions are produced by dissociative photoionization of O₂ at photon energies larger than the first threshold, 18.73 eV, leading to the production of ground state O⁺(⁴S) and O(³P). At higher photon energies, various combinations of O⁺ and O electronic ground or excited states associated with the asymptotic dissociation limits shown in Table 1 can be formed.

Two types of experiments have been performed. In the “continuous” mode, all the DC potentials are fixed and all parent O⁺ ions, whatever their internal energy, are allowed to react. By the choice of the photon energy, distribution of O⁺ ions can be produced either in their pure ⁴S ground state (below 22.06 eV) or in a mixed population of ⁴S and ²D (between 22.06 and 23.75 eV) or ⁴S, ²D and ²P states (above 23.75 eV). Although the O⁺ excitation is not purely defined (except for O⁺(⁴S) below 22.06 eV), these experiments are very useful to identify the differences between the reactivity of O⁺ in its different electronic states, in particular changes in the branching ratio between products.

In the second type of experiments, called the “TPEPICO” mode, pure populations of O⁺(⁴S), O⁺(²D) or O⁺(²P) are prepared in the following way. For a dissociative photoionization process at a given photon energy $h\nu$:

the available energy after the photoionization is distributed among $E_{\text{int}}(\text{O}_2^+)$, the internal energy of O₂⁺, and $E_{\text{k}}(\text{e}^-)$, the kinetic energy of the photoelectron, according to:

$$h\nu - \text{IP}(\text{O}_2) = E_{\text{int}}(\text{O}_2^+) + E_{\text{k}}(\text{e}^-) \quad (2)$$

showing that if a class of photoelectrons of a given kinetic energy is selected, the O_2^+ excitation energy can be controlled. The TPEPICO technique used here consists in selecting only the events associated with threshold electrons, i.e. of kinetic energy lower than 15 meV typically. A first selection of slow electrons is achieved by discriminating the fast electrons geometrically, by extracting the electrons from the center of the source with a small electric field of about 1 V/cm through a small hole of 2 mm diameter. A further temporal selection is achieved by selecting only those photoelectrons arriving within a window of 5 ns centered around the arrival time of threshold electrons (calibrated using threshold electrons produced in the photoionization of Ar at its first ionization threshold $Ar^+(^2P_{3/2})$). The temporal discrimination is possible only in the 8 bunch mode of SOLEIL set for 6 days per semester only, in which two consecutive bunches of electrons in the storage ring, and hence two photon pulses, are separated by 148 ns. For the reference time of the electron TOF, a periodic TTL pulse (148 ns period) provided by the SOLEIL electronics (TIMBLE device) and coincident, with the help of an adjustable delay, to the photon bunch arrival time in CERISES is used.

After the dissociation process, the O_2^+ internal energy is redistributed among the internal energy and released kinetic energy of O^+ and O according to :

$$h\nu - IP(O_2) - E_k(e^-) - D_0(O^+ - O) = E_{int}(O^+) + E_{int}(O) + E_k(O^+) + E_k(O) \quad (3)$$

where $D_0(O^+ - O)$ is the dissociation energy of O_2^+ . Therefore, to control the internal energy of O^+ and O, i.e. to know which asymptote of Table 1 is reached, not only $E_k(e^-)$ but also the recoil kinetic energy of O^+ and O must be known. As a consequence, in a similar way to the one used to discriminate fast electrons, the fast O^+ ions were discriminated and only the events associated

with no recoil energy of $O^+ + O$ were selected by extracting the ions in the opposite side of the photoelectrons with the same small field (1 V/cm) through a small hole of 2 mm diameter too.

The O^+ events recorded in coincidence with threshold photoelectrons are displayed in Figure 3 as a function of photon energy in regions close to the three asymptotes # 1, 3 and 5 associated with the production of O^+ in its 4S , 2D and 2P state, respectively, and $O(^3P)$. The yield shown is the difference between coincidences recorded by triggering the extraction of O^+ ions by a “start” signal which is either a threshold photoelectron detection (for “true + false” coincidences) or a random signal (for “false” coincidences). Reduction of false coincidences was greatly improved by using a sweeping electrode in the center of the source that was stopped when an electron is detected and by using a second pulsed electrode, also triggered by the detection of an electron, which transmits the ions only during a reduced time.

Figure 3. TPEPICO spectrum of O^+ ions produced by dissociative photoionization of O_2 . The labels 1-6 correspond to the positions of dissociation limits given in Table 1.

As shown, a high yield of TPEPICO events is observed with a maximum at the expected thresholds of the three asymptotes. Above the thresholds, the yield is decreasing because the O^+ ions and O atoms are still formed in the same states but with a recoil kinetic energy increasing

with photon energy and are hence geometrically discriminated. It is important to note that, at photon energies just below the thresholds, the yield is essentially zero because the O^+ ions produced in states corresponding to lower asymptotes, i.e. with large kinetic energy, are completely discriminated. This guarantees that, at the maximum of each of the peaks 1, 3 and 5, the measured O^+ yield has no contribution from lower asymptotes and, consequently, is constituted of pure population of 4S , 2D and 2P state respectively.

In this “TPEPICO” mode, the reactivity of state-selected $O^+(^4S, ^2D, ^2P)$ ions is measured with a photon energy fixed at each of the three thresholds of interest. As announced in the former subsection, at these photon energies, the O^+ ion recoil energy is close to zero and does not contribute to the broadening of the collision energy. Moreover, as already mentioned, the extraction of O^+ ions is triggered by threshold electrons and hence the TPEPICO mode is naturally pulsed. This allows the measurements of parent and product ion TOFs on a window time of 2 ms. After a careful calibration of potentials and lengths of QI, OI, OII and QII, an inversion procedure of the measured TOFs can be undertaken which leads to the determination of the velocity of the ions when they are produced in the reaction cell. More precisely, only the distributions of their axial velocity component along the main longitudinal axis of the octopoles can be extracted in our configuration, but this determination is nevertheless very helpful for the characterization of the reaction dynamics.

RESULTS

Choice of the system

^{18}O or D isotope substitution is useful to overcome mass overlaps between parents, primary products and secondary products. The nature of the main and minor products of the secondary

reactions that could occur here has already been discussed in detail by Levandier et al (see Table 1 of their work³⁸). In particular, as CH_4^+ and CH_3^+ ions are the two major product ions (see following subsections), it is important to consider products from the $\text{CH}_4^+ + \text{CH}_4$ and $\text{CH}_3^+ + \text{CH}_4$ reactions, mainly leading to CH_5^+ and C_2H_5^+ secondary ions. Given these considerations, it appears that the $^{18}\text{O}^+ + \text{CH}_4$ system is the one providing the smallest number of these overlaps. Nevertheless, even this system has two drawbacks. As water is always present in the vacuum system of CERISES, part of the parent ions selected with QI at m/z 18 could be constituted of H_2O^+ ions. In our “continuous” mode of operation, this could be a problem, especially for the $^{18}\text{OH}^+$ product of the $^{18}\text{O}^+ + \text{CH}_4$ reaction at m/z 19 overlapping with H_3O^+ which is the main product of the $\text{H}_2\text{O}^+ + \text{CH}_4$ reaction. In the “TPEPICO” mode however, as parent ions are extracted in coincidence with threshold electrons, the potential contamination of $^{18}\text{O}^+$ parent ions by H_2O^+ ions is very much reduced, as shown below. This is the reason why this system has been used in some of the measurements. The second drawback concerns CH_4^+ ions whose mass is just two masses below the parent ion mass $^{18}\text{O}^+$. Indeed, as the asymmetry of the mass peak lies mainly on the low-mass edge, the contribution from the tail of the much stronger parent ion signal to the CH_4^+ mass peak is a difficult problem to overcome, especially when the collision energy is increased, unless by reducing drastically the sensitivity. Thus, although at first sight, the $^{16}\text{O}^+ + \text{CD}_4$ reaction system,³⁸ is not ideal considering mass overlaps it appeared to be the best choice to determine the nature of the major product ions in the state-selected “TPEPICO” mode.

Cross sections of the $\text{O}^+(\text{}^4\text{S}, \text{}^2\text{D}, \text{}^2\text{P})$ state-selected reactions

Measurement overview

The experiments carried out in the “continuous” mode for the $^{16}\text{O}^+ + \text{CD}_4$ system, indicate that at photon energies below 20.06 eV, i.e. for ground state $\text{O}^+(\text{}^4\text{S})$, the major product ions are observed at mass m/z 20 while they are observed at mass m/z 18, at higher photon energies when a fraction of the O^+ population is excited in either the $\text{}^2\text{D}$ or $\text{}^2\text{P}$ state. These masses correspond to $\text{CD}_4^+/\text{D}_2\text{O}^+$ and $\text{CD}_3^+/\text{OD}^+$ ions respectively, directly resulting from the primary reaction^{35, 38} of O^+ with CD_4 .^{35, 38} Therefore, parent and product TOF have been recorded in the “TPEPICO” mode, for masses m/z 16, 18 and 20 at photon energies of 18.73, 22.06 and 23.75 eV, corresponding respectively, to the reactions of pure $\text{O}^+(\text{}^4\text{S})$, $\text{O}^+(\text{}^2\text{D})$ and $\text{O}^+(\text{}^2\text{P})$ for three different conditions of collision energies, $E_{\text{CM}} = 0.2, 0.7$ and 5 eV. The acquisition time of a “true + false” coincidence TOF is typically 400 s for the parent ion and 4000 s for a product ion. False coincidence TOFs are recorded during a time corresponding to the same number of “starts” (i.e. O^+ extraction triggering) as for the corresponding “true + false” coincidence TOF. The rate of false coincidence is kept below 10 % typically by reducing the photon flux or the dioxygen pressure in the source. A selection of the recorded TOFs after subtraction of the false coincidences is shown in Figure 4. From the ratio of product to parent TOF areas and the known pressure of the deuterated methane target, absolute reaction cross sections are derived and displayed in Figures 5-7 as well as the sum and branching ratios for the production of $\text{CD}_4^+/\text{D}_2\text{O}^+$ and $\text{CD}_3^+/\text{OD}^+$ in Figure 8. The error bars indicated on Figures 5-7 for this work correspond to the quadratic sums of the statistical errors on the number of counts and 10% uncertainty on the determination of the absolute target pressure, while for the experimental points retrieved from the literature the uncertainties are estimated to be between ± 20 and ± 30 % by the authors.^{35, 38} As already mentioned, secondary reactions of the major primary products lead to additional ionic products, in particular CD_5^+ and C_2D_5^+ arising from the reactions of CD_4^+ and CD_3^+ with CD_4

respectively. The ratios between secondary and primary products, $\text{CD}_5^+/\text{CD}_4^+$ and $\text{C}_2\text{D}_5^+/\text{CD}_3^+$, measured in the “continuous” mode were always found to be within a 20 to 30 % range depending on the collision energy and the target pressure used. Due to the limited amount of time available for coincidence experiments at the SOLEIL synchrotron, CD_5^+ and C_2D_5^+ were not measured in the “TPEPICO” mode. The cross sections reported in Figures 5-7 for the primary products are not corrected from these secondary productions. In order to do it, a correction factor of 1.25 would have to be applied. Nevertheless, Levandier et al.³⁸ did not make such corrections either and thus their measurements can be directly compared with the presented data as both experiments have been conducted within the same target pressure range, i.e. $0.8 - 1.0 \cdot 10^{-4}$ Torr.

Figure 4. TOF spectra after subtraction of the false coincidence events of O^+ parent ions (top), CD_4^+/D_2O^+ (middle) and CD_3^+/OD^+ (bottom) product ions for the reaction of $O^+(^4S) + CD_4$ at a collision energy in the CM frame $E_{CM} = 0.2$ eV (left), $O^+(^2D) + CD_4$ at $E_{CM} = 0.7$ eV (center) and $O^+(^2P) + CD_4$ at $E_{CM} = 5.0$ eV (right).

Reaction of $O^+(^4S)$ ground state ions

Figure 5. Absolute reaction cross sections for the production of CD_4^+/D_2O^+ or CH_4^+ ions (blue line and squares) and CD_3^+/OD^+ or CH_3^+ ions (red line and circles) for the reaction of $O^+(^4S)$ with CD_4 or CH_4 as a function of collision energy. Solid symbols: this work for $O^+(^4S) + CD_4$ in the TPEPICO mode; solid line: Levandier et al study³⁸ for $O^+(^4S) + CD_4$; open symbols: Ottinger et al study³⁵ for $O^+(^4S) + CH_4$ (dotted lines are drawn just to guide the eye). The reported uncertainties are $\pm 30\%$ and $\pm 20\%$ by Levandier³⁸ and Ottinger³⁵ respectively.

For the reaction of ground state $O^+(^4S)$ with CD_4 , the main products observed in the “TPEPICO” mode at all collision energies are by far ions at m/z 20 as already found by Levandier et al.³⁸ The agreement between the two experiments is good within error bars at the two lowest collision

energies, yet our value seems to be somehow lower at 5 eV collision energy. The ions at m/z 20 are essentially produced by the charge transfer process (O1) and thus mainly correspond to CD_4^+ ions at all collision energies, except at very low energy where a smaller contribution to the signal is attributable to deuterated water ions, D_2O^+ (O7).³⁸ This contribution is expected to decrease very rapidly with collision energy, as suggested by the observation of an $(E_{\text{CM}})^{-0.47}$ dependence of the H_2O^+ signal at m/z 18 measured for the $\text{O}^+(\text{}^4\text{S}) + \text{CH}_4$ reaction³⁸ and indicating that this reaction - in which two bonds are broken and two new bonds are formed - goes through a long-lived complex as also confirmed by the symmetric velocity distribution of H_2O^+ ions with respect to V_{CM} observed at $E_{\text{CM}} = 0.5$ eV.³⁸

We have evaluated the relative contribution of the water ion formation channel (O7) to the charge transfer one (O1) at low collision energy ($E_{\text{CM}} = 0.17$ eV) by measuring the cross section for $\text{H}_2^{18}\text{O}^+$ production in the $^{18}\text{O}^+(\text{}^4\text{S}, \text{}^2\text{D}, \text{}^2\text{P}) + \text{CH}_4$ reaction in the TPEPICO mode. However, as already mentioned, a possible contamination of $^{18}\text{O}^+$ ions at m/z 18 by $\text{H}_2^{16}\text{O}^+$ ions coming from water traces present in the experiment cannot be excluded. Therefore, before looking at this reaction, the potential pollution by water ions to O^+ parent ions has been evaluated in the “TPEPICO” mode, by putting $^{16}\text{O}_2$ in the source but no target gas in the reaction cell and recording coincidence signals at masses m/z 16 ($^{16}\text{O}^+$) and 18 ($\text{H}_2^{16}\text{O}^+$). Given that the natural abundance of ^{18}O is 0.2% of all oxygen atoms, these control experiments conducted at the three photon energies, 18.73, 22.06 and 23.75 eV, have led us to conclude that the $\text{H}_2^{16}\text{O}^+ / ^{16}\text{O}^+$ ratio, in the “TPEPICO” mode, is lower than 0.3 % for the $\text{O}^+(\text{}^4\text{S})$, $\text{O}^+(\text{}^2\text{D})$ and $\text{O}^+(\text{}^2\text{P})$ states. Thus, since the $^{18}\text{O}^+$ and $^{16}\text{O}^+$ parent ion production efficiency is expected to be the same in this mode, a significant contribution of reactions of $\text{H}_2^{16}\text{O}^+$ ions to the product yield observed when $^{18}\text{O}^+$ reacts with methane can be ruled out. So let us consider the results obtained in the “TPEPICO”

mode for the reactive $^{18}\text{O}^+ + \text{CH}_4$ system. These measurements have shown that a measurable amount of $\text{H}_2^{18}\text{O}^+$ ions at m/z 20 is obtained only for the ground state reaction, i.e. reaction of methane with $^{18}\text{O}^+(\text{}^4\text{S})$. The corresponding reaction cross section at $E_{\text{CM}} = 0.17$ eV has been estimated to $28 \text{ \AA}^2$, that is about a third of the cross section retrieved for the production of $\text{CD}_4^+/\text{D}_2\text{O}^+$ ($81 \text{ \AA}^2$) we measured for the $\text{O}^+(\text{}^4\text{S}) + \text{CD}_4$ reaction at $E_{\text{CM}} = 0.2$ eV. Note also that, in the low energy range ($0.08 - 0.2$ eV), lower values (between 18 and $12 \text{ \AA}^2$) have been found by Levandier et al for the H_2O^+ production cross section in the $^{16}\text{O}^+(\text{}^4\text{S}) + \text{CH}_4$ reaction.³⁸

Much lower cross sections have been obtained in the “TPEPICO” mode for the production of m/z 18 ions ($\text{CD}_3^+/\text{OD}^+$) in the $\text{O}^+(\text{}^4\text{S}) + \text{CD}_4$ reaction and were also found to be in reasonable agreement with the values measured by Levandier et al.³⁸ As visible in Figure 5, the relative difference is higher for the lowest collision energy (about $2 \text{ \AA}^2$ compared to $4 \text{ \AA}^2$) but, for this system, these values are at the limit of our sensitivity in the TPEPICO mode as can be inferred from the error bars. The formation of these $\text{CD}_3^+/\text{OD}^+$ ions can be accounted for, either by the hydride transfer (O2), the dissociative charge transfer (O3) or the D transfer (O4). The importance of these channels as a function of collision energy has been thoroughly discussed for the reaction of ground state $\text{O}^+(\text{}^4\text{S})$ ions by Levandier et al, in particular with respect to spin-allowed or spin-forbidden mechanisms.³⁸ One of the important points is that, though other mechanisms are not precluded, the dissociative charge transfer (O3), which is the only endothermic channel (0.71 eV) among the three, is fully consistent both, with the increase of the cross section above 0.5 eV, and the observation of the product distribution essentially backscattered at thermal velocities in the laboratory frame for the highest collision energies.

The cross sections measured by Ottinger et al for the production of CH_4^+ and CH_3^+ in the $\text{O}^+(\text{}^4\text{S}) + \text{CH}_4$ reaction at collision energies of 2 , 5 and 15 eV are also indicated³⁵ in Figure 5. In this

experiment, the parent O^+ ions are produced in a discharge for different values of the ion-source voltage (U_A) depending on the amount of metastable species desired. At $U_A = 40$ V, the fraction of excited metastable species (2D or 2P) is estimated to be 3 %, and thus the O^+ ions are essentially in their ground state 4S . Note that, though no isotopic labeling is used, they managed to distinguish the O^+ parent ions from CH_4^+ products at m/z 16, and also OH^+ primary products from CH_5^+ secondary products (coming from the reaction of CH_4^+ primary products) at m/z 17. The differentiation of these ions was possible because their kinetic energy distributions, which were also measured in this study, are well separated, at least at these relatively high collision energies (2-15 eV). Note also that the CH_4 target pressures used in their experiments range from $2 \cdot 10^{-4}$ to $3 \cdot 10^{-3}$ Torr, i.e. are higher by at least a factor 2 from our conditions, but that the cross sections are derived from an analysis of the pressure dependence and its extrapolation to the low range limit. Cross sections lower than $1 \text{ \AA}^2$ are measured for the OH^+ ions production.³⁵ As visible in Figure 5, the values obtained for CH_4^+ and CH_3^+ productions over the 2-15 eV collision energy range are in good agreement with the cross sections measured by Levandier et al³⁸ and those obtained in this work for the $O^+(^4S) + CD_4$ reaction at target pressures between 0.8 and $1.0 \cdot 10^{-4}$ Torr. Note however that, although being still within the error bar limits, our measured value for CD_4^+ production for $E_{CM} = 5$ eV is a bit smaller than Levandier et al³⁸ and Ottinger et al³⁵ values.

Reaction of $O^+(^2D)$ and $O^+(^2P)$ metastable ions

When O^+ ions are prepared in the first (2D) or second (2P) metastable state, the branching ratio between CD_4^+/D_2O^+ and CD_3^+/OD^+ products is completely inverted, compared to the case of O^+ ions in the ground state (4S), in favor of CD_3^+/OD^+ , going from 10 to 77 and 78 % (on average on the three collision energies) respectively, whereas the sum of the two absolute cross sections

slightly decreases from 70 to 60 and 43 Å², as can be seen in Figures 6-8. For both O⁺(²D) and O⁺(²P) reactions, the formation of the major products, CD₃⁺/OD⁺, decreases slowly with collision energy but much less strongly than for the (E_{CM})^{-1/2} dependence characteristic of the Langevin capture cross sections. As for the formation of the charge transfer product, CD₄⁺, for the O⁺(⁴S) reaction, these behavior is an indication of a direct exothermic process occurring at relatively long distances.

Figure 6. Absolute reaction cross sections for the production of CD₄⁺/D₂O⁺ or CH₄⁺ ions (blue squares) and CD₃⁺/OD⁺ or CH₃⁺ ions (red circles) as a function of collision energy (dotted lines are drawn just to guide the eye). Solid symbol: this work for the reaction of pure O⁺(²D) with CD₄ in the TPEPICO mode; open symbol: Ottinger et al study³⁵ for the reaction O⁺(²D+²P) with CH₄ (see text for details). The uncertainties reported by Ottinger³⁵ are ± 30%.

It is very important to note that the total energy in the system is about the same for the O⁺(⁴S) + CD₄ reaction at E_{CM} = 5 eV and the O⁺(²P) + CD₄ reaction at E_{CM} = 0.2 eV, as the excitation energy of the ²P state is 5.017 eV relative to the ⁴S state. However, if we compare the two sets of

measurements in Figures 5 and 7, the branching ratio between $\text{CD}_4^+/\text{D}_2\text{O}^+$ and $\text{CD}_3^+/\text{OD}^+$ products are clearly inversed, indicating that internal energy and collision energy have very different effects on the reaction dynamics.

Figure 7. Absolute reaction cross sections for the production of $\text{CD}_4^+/\text{D}_2\text{O}^+$ or CH_4^+ ions (blue squares) and $\text{CD}_3^+/\text{OD}^+$ or CH_3^+ ions (red circles) as a function of collision energy (dotted lines are drawn just to guide the eye). Solid symbols: this work for the reaction of pure $\text{O}^+(^2\text{P})$ with CD_4 in the TPEPICO mode; open symbols: Ottinger et al study³⁵ for the reaction $\text{O}^+(^2\text{D}+^2\text{P})$ with CH_4 (see text for details). The uncertainties reported by Ottinger³⁵ are $\pm 30\%$.

In Figures 6 and 7, we have added for comparison the cross sections reported by Ottinger et al at collision energies of 2, 5 and 15 eV for the production of CH_4^+ and CH_3^+ in the reaction of $\text{O}^+(^2\text{D} + ^2\text{P})$ ions with CH_4 .³⁵ These values have been inferred from the analysis of two experiments. In the first one, already described above, $\text{O}^+(^4\text{S})$ ground state ions are produced with a very small fraction (about 3 %) of excited metastable species $\text{O}^+(^2\text{D}, ^2\text{P})$ by setting the ion-source voltage at $U_A = 40$ V. In the second experiment, U_A is raised to 90 V, for which a much higher fraction of

metastable states (about 30-35 %) is produced together with $O^+(^4S)$ ground state ions. This composition, on the contrary to former experiments with the same source where it was directly measured,¹⁹ was assumed here by making various hypotheses on the proportion of metastable states while analyzing the coherence of the inferred cross sections.³⁵ The best values for the fraction of $^2D + ^2P$ metastable states, consistent with the two sets of data at $U_A = 40$ and 90 V, was found to be 3 % and 30-35 % respectively, but no information on the relative proportions of $^2D / ^2P$ states for these two experimental conditions can be given.³⁵ With these assumed compositions, the cross sections for the $O^+(^2D + ^2P) + CH_4$ reaction, shown in Figures 6-7, have been inferred from the cross sections measured in the two experiments at $U_A = 40$ and 90 V.³⁵ As can be seen in Figure 6, at 5 eV collision energy, our CD_3^+/OD^+ cross section measurement for the reaction of O^+ ions, prepared in pure 2D population, with CD_4 is in good agreement with the CH_3^+ cross section reported by Ottinger et al for the reaction of O^+ ions in a mixed $^2D + ^2P$ composition with CH_4 ,³⁵ whereas our measurement for the reaction of O^+ ions, prepared in pure 2P population (see Figure 7) is a bit lower than their value. This could be an indication that a larger fraction of the 2D state than the 2P state are produced in their discharge at $U_A = 90$ V. This seems reasonable according to former results they obtained for a close value of the ion-source voltage, $U_A = 80$ V,¹⁹ and where $^4S: ^2D: ^2P$ compositions were found to be $0.86 : 0.09 : 0.05$ and $0.63 : 0.22 : 0.15$, for two different source pressures, corresponding to $^2D: ^2P$ relative ratios of $64 : 36$ % and $60 : 40$ % respectively.

We have shown above, that complementary cross section measurements can be done safely in the TPEPICO mode for the $^{18}O^+ + CH_4$ reaction. In this mode, we found that $H_2^{18}O^+$ and $^{18}OH^+$ productions in the $^{18}O^+(^2D \text{ or } ^2P) + CH_4$ reactions are very small, below our sensitivity limit. So, if we consider that $^{18}O^+ + CH_4$ and $^{16}O^+ + CD_4$ reactions behave similarly, i.e. that isotope effects

can be neglected, then the products observed in the $^{16}\text{O}^+(\text{}^2\text{D}, \text{}^2\text{P}) + \text{CD}_4$ reaction at m/z 20 and 18 correspond essentially to CD_4^+ and CD_3^+ ions, respectively.

Among the various products identified by Levandier et al in the reaction of $\text{O}^+(\text{}^4\text{S})$ ground state, there are products such as HCO^+ , H_2CO^+ and H_3CO^+ (or their deuterated equivalents), corresponding to the (O8-O10) channels, where a new C-O bond is formed. Their measured velocity distributions centered on V_{CM} , the mass center velocity, confirm that their production can be accounted for by the decomposition of the full complex, H_4CO^+ , or possibly, for HCO^+ , by the dissociation of intermediate complexes like H_2CO^+ or H_3CO^+ .³⁸ As $\text{HCO}^+/\text{DCO}^+$ ions are by far the most abundant of this class of products, we have looked at the possible formation of DCO^+ products in the reaction of excited $\text{O}^+(\text{}^2\text{D}, \text{}^2\text{P})$ ions with CD_4 in the “TPEPICO mode” and found that the cross sections for the production of ions at mass m/z 30 at $E_{\text{CM}} = 0.17$ eV is very low, 8 and 6 Å² for the $\text{O}^+(\text{}^2\text{D}) + \text{CD}_4$ and $\text{O}^+(\text{}^2\text{P}) + \text{CD}_4$ reactions respectively. Yet, before making any conclusion about the DCO^+ ion production, we should first discuss the possibility of the contribution of other ions to the signal at mass m/z 30. Indeed, apart from DCO^+ ions, the signal at m/z 30 can also be accounted for, in principle, by C_2D_3^+ production. This ion is a minor product from the secondary reaction of CD_2^+ with CD_4 . However, as CD_2^+ ion production is limited as shown below, the production of C_2D_3^+ by this mechanism is not very probable. It is also a minor product from the secondary reaction of CD_3^+ with CD_4 , but as CD_3^+ is the main primary product, contrary to CD_2^+ , this process should be considered. This reaction is endothermic and necessitates about 1 eV of extra energy to occur but this energy can be brought either as collision energy as shown by Clow et al⁵⁹ or as vibrational excitation of the methyl cations as shown in one of our very recent work.⁶⁰ The analysis of CD_3^+ product velocity below (following section) shows that this ion is formed at thermal velocities, thus does not have

sufficient kinetic energy to react efficiently with CD_4 to form C_2D_3^+ ions. Formation of CD_3^+ ions with more than 1 eV vibrational excitation cannot be excluded however, and their reaction with CD_4 , leading to C_2D_3^+ ions, could partly account for the ions observed at mass m/z 30. Yet, if we consider a scenario in which all the products observed at mass m/z 30 correspond to DCO^+ ions, i.e. with no contribution from C_2D_3^+ ions, then the cross sections measured remain small and we can conclude that DCO^+ do not become a major product of the $\text{O}^+ + \text{CD}_4$ reaction upon excitation of the O^+ parent ions in the (^2D) or (^2P) metastable states.

Figure 8. Sum (solid symbol and left scale) of the absolute reaction cross sections for the production of $\text{CD}_4^+/\text{D}_2\text{O}^+$ and $\text{CD}_3^+/\text{OD}^+$ measured in the TPEPICO mode as a function of collision energy for the reaction of $\text{O}^+(^4\text{S})$ (circles), $\text{O}^+(^2\text{D})$ (squares) and $\text{O}^+(^2\text{P})$ (triangle) with CD_4 . The branching ratios $\text{CD}_3^+/\text{OD}^+ / (\text{CD}_4^+/\text{D}_2\text{O}^+ + \text{CD}_3^+/\text{OD}^+)$ are displayed with open symbols on the right scale.

As will be discussed in the following section, dissociative charge transfer (O3) could be the main channel accounting for the very efficient production of CD_3^+ ions in the reaction of the $\text{O}^+(^2\text{D})$ and $\text{O}^+(^2\text{P})$ excited ions with CD_4 . The energy diagram in Figure 1 shows that O^+ excitation to

the first two metastable states opens thermodynamically feasible channels, leading to the $\text{CH}_3^+ + \text{H} + \text{O}$ products in various excited states. We can also see that several channels associated with the second dissociative charge transfer (O6) leading to $\text{CH}_2^+ + \text{H}_2 + \text{O}$ products are also energetically accessible in the same energy range, though slightly above the former dissociative charge transfer channels (O3), leading to $\text{CH}_3^+ + \text{H} + \text{O}$, by about 0.8 eV. It is interesting to know how the two dissociative charge transfer channels (O3) and (O6) compete. Note that the $^{16}\text{O}^+ + \text{CD}_4$ reaction cannot be used for this purpose as CD_2^+ ions have the same mass as the $^{16}\text{O}^+$ parent ion. So, to quantify more accurately the ratio between CH_2^+ and CH_3^+ products, we have measured their yields as a function of collision energy, for the $^{18}\text{O}^+ + \text{CH}_4$ reaction, in the “continuous” mode at $h\nu = 18.78$ and 22.25 eV, i.e. in conditions where the O^+ parent ions are formed either in pure ^4S state or in a mixture of both ^4S and ^2D states. The derived cross sections, $\sigma_{4\text{S}}(\text{CH}_2^+)$, $\sigma_{4\text{S}}(\text{CH}_3^+)$, $\sigma_{\text{MIX}}(\text{CH}_2^+)$ and $\sigma_{\text{MIX}}(\text{CH}_3^+)$, as well as the $\text{CH}_2^+ / \text{CH}_3^+$ ratio are shown in Figure 9, (in panel (a) and (b) respectively). We see that, varying with collision energy, $\sigma_{\text{MIX}}(\text{CH}_2^+)$ is higher than $\sigma_{4\text{S}}(\text{CH}_2^+)$, but their ratio to $\sigma(\text{CH}_3^+)$ is small, with a maximum at 14 %. To estimate what happens for the $^{18}\text{O}^+(^2\text{D}) + \text{CH}_4$ reaction, we have first determined the fraction, $f_{2\text{D}}$, of the O^+ ions formed in the ^2D state in the experiment performed at 22.25 eV. To do so, we have used the fact that the cross sections for the reaction of the mixed $(1 - f_{2\text{D}}) ^4\text{S} + f_{2\text{D}} ^2\text{D}$ population of $^{18}\text{O}^+$ ions can be expressed as:

$$\sigma_{\text{MIX}}(\text{CH}_3^+) = \sigma_{4\text{S}}(\text{CH}_3^+).(1 - f_{2\text{D}}) + \sigma_{2\text{D}}(\text{CH}_3^+).f_{2\text{D}} \quad (4)$$

$$\sigma_{\text{MIX}}(\text{CH}_2^+) = \sigma_{4\text{S}}(\text{CH}_2^+).(1 - f_{2\text{D}}) + \sigma_{2\text{D}}(\text{CH}_2^+).f_{2\text{D}} \quad (5)$$

where $\sigma_{2\text{D}}(\text{CH}_3^+)$ and $\sigma_{2\text{D}}(\text{CH}_2^+)$ is the cross section for production of CH_3^+ and CH_2^+ in the $^{18}\text{O}^+(^2\text{D}) + \text{CH}_4$ reaction. To determine $f_{2\text{D}}$ from Equation (4), we have replaced the unknown

$\sigma_{2D}(\text{CH}_3^+)$ value by the cross section measured in the “TPEPICO” mode for $\text{CD}_3^+/\text{OD}^+$ production in the $\text{O}^+(\text{}^2\text{D}) + \text{CD}_4$ reaction. As we have shown above that the contribution of OD^+ ions to the products observed at m/z 18 is small for the reaction of $\text{O}^+(\text{}^2\text{D}, \text{}^2\text{P})$ with CD_4 , this is a good approximation if isotope effects are neglected. Hence, three values for f_{2D} , 0.219, 0.273 and 0.270 have been derived from Equation (4), each one for the collision energies, 0.2, 0.7 and 5 eV, at which $\text{CD}_3^+/\text{OD}^+$ cross sections have been measured in the “TPEPICO” mode. As the three values found for f_{2D} are very similar and thus consistent, a mean value of 0.254 has been used for f_{2D} to calculate the $\sigma_{2D}(\text{CH}_3^+)$ and $\sigma_{2D}(\text{CH}_2^+)$ cross sections from Equations (4) and (5), at all collision energies for which the “continuous” mode experiments were conducted. The results are shown in Figure 9 as dashed lines (cross sections in panel (a) and ratio in panel b).

Figure 9. Reaction cross sections (Panel **(a)**) for the production of CH_2^+ (green thin lines) and CH_3^+ (thick red lines) and ratios $\text{CH}_2^+/\text{CH}_3^+$ (Panel **(b)**) measured in the “continuous” mode for the $^{18}\text{O}^+(^4\text{S}) + \text{CH}_4$ reaction at $h\nu = 18.78$ eV (dotted lines) and the $^{18}\text{O}^+((1-f_{2\text{D}}).^4\text{S} + f_{2\text{D}}.^2\text{D}) + \text{CH}_4$ reaction at $h\nu = 22.25$ eV (solid lines), and deduced from the analysis (dashed lines) for the $^{18}\text{O}^+(^2\text{D}) + \text{CH}_4$ reaction (see text for details). Cross sections for $\text{CD}_3^+/\text{OD}^+$ production in the $\text{O}^+(^2\text{D}) + \text{CD}_4$ reaction measured in the “TPEPICO” mode (solid red circles in Panel a) have been used for the analysis.

As expected from the method used, the calculated $\sigma_{2\text{D}}(\text{CH}_3^+)$ cross sections are close to the ones measured in the “TPEPICO” mode, but the good agreement for the three collision energies stems from the fact that the mean $f_{2\text{D}}$ value used in the calculation is close from the three determined values. The values found for $\sigma_{2\text{D}}(\text{CH}_2^+)$ lie between 6 and 8 Å², i.e. much higher than the ones measured for $\sigma_{4\text{S}}(\text{CH}_2^+)$ values. This increase might be the indication that CH_2^+ ions are formed, for the reaction of $\text{O}^+(^4\text{S})$ ions, through the channel (O5), $\text{CH}_2^+ + \text{H}_2\text{O}$, which is exothermic, and, for the reaction of $\text{O}^+(^2\text{D})$ ions, through the dissociative charge transfer channel (O6), $\text{CH}_2^+ + \text{H}_2 + \text{O}$, which is energetically opened only with additional O^+ electronic excitation. For the reaction of $\text{O}^+(^2\text{D})$, these measurements place the CH_2^+ channel less than a factor 2 lower than the charge transfer channel except for the highest collision energy (5 eV) where they become of comparable importance. Note however that the ratio $\sigma_{2\text{D}}(\text{CH}_2^+) / \sigma_{2\text{D}}(\text{CH}_3^+)$ stays low, close from 15%, at all collision energies, meaning that CH_3^+ ions remains the main product of the $\text{O}^+(^2\text{D}) + \text{CH}_4$ reaction.

Axial product velocity distributions

From the TOF inversion procedure described in the experimental section, the ionic product axial velocity distributions $P(v_z')$ along the main z axis of the octopoles have been determined for the main products and displayed in Figure 10. To analyze the reaction dynamics from the product velocity distributions, useful reference velocities are also indicated in Figure 10.

Figure 10. Axial product velocity distributions in the LAB frame calculated by inversion of the recorded TPEPICO TOFs for the $O^+(^4S) + CD_4$ reaction and CD_4^+/D_2O^+ products (left column), the $O^+(^2D) + CD_4$ reaction and CD_3^+/OD^+ products (center column) and the $O^+(^2P) + CD_4$ reaction and CD_3^+/OD^+ products (right column), at a collision energy $E_{CM} = 0.2$ eV (top), 0.7 eV (middle), and 5.0 eV (bottom). The dotted black line indicates V_{CM} , the velocity of the center of mass, and dashed lines correspond to lower and upper limits for the following assumptions: all

the available energy goes into product kinetic energy (black dashed line), no variation of kinetic energy between reactants and products (blue dashed line), resonant charge transfer (red dashed line) (see text for details).

The first reference velocity to consider is the velocity of the center of mass, V_{CM} , indicated as a dotted black line in fig. 10. It is indeed important for products resulting from the decomposition of a long-lived complex since velocity distributions are expected to be symmetric relative to V_{CM} in that case. It is also of interest, when very small amounts of energy are available for product kinetic energy, because, in that case, the product velocity is necessarily very small in the CM frame, so very close from V_{CM} in the laboratory frame. The special scenario in which 100 % of the available energy is distributed as kinetic energy must also be considered and the corresponding velocity limits $V_{\pm}(\Delta E_{CM} \text{ Max})$ are thus indicated as black dashed lines. These limits are especially useful to estimate which fraction of the available energy is distributed as kinetic energy in exothermic processes. At the opposite of these two mechanisms, there is also the possibility for resonant mechanisms in which no exchange of kinetic energy between reactant and products occurs. The corresponding velocity limits $V_{\pm}(\Delta E_{CM}=0)$, are indicated in Figure 10 as blue dashed lines. The red dashed lines indicating the particular values of 0 and $2 \cdot V_{CM}$ correspond to these latter limits for the special case of charge transfer, for which there is no exchange of masses either.

For the $O^+(^4S) + CD_4$ reaction (left column in Figure 10), two ions: CD_4^+ and D_2O^+ could contribute to the signal at m/z 20. The limits $V_{\pm}(\Delta E_{CM} \text{ Max})$ have been calculated for the process $O^+(^4S) + CD_4 \rightarrow CD_4^+ + O$, but the exothermicity for the production of $D_2O^+ + CD_2$ is about the same and the limit calculated for this channel is very close (0.17 instead of 0.16 cm/ μ s for

instance at $E_{\text{CM}} = 0.2$ eV). The velocity distribution observed for $E_{\text{CM}} = 0.2$ eV has a strong backward component in the CM frame (velocities lower than V_{CM} in the laboratory frame) and is an evidence that CD_4^+ ions are produced by the charge transfer process (O1). However, a second component more centered on V_{CM} and extending up to the $V_{\pm}(\Delta E_{\text{CM}} \text{ Max})$ limit is visible and should be associated with the production of D_2O^+ ions but for low collision energies only. This last component is indeed reduced and further suppressed at higher energies as can be seen at 5 eV collision energy where only the near thermal velocity component is visible.

For the $\text{O}^+(\text{}^2\text{D}, \text{}^2\text{P}) + \text{CD}_4$ reactions (center and right columns in Figure 10), among the two ions, CD_3^+ and OD^+ , that could contribute in principle to the signal at mass m/z 18, only the methyl cation is efficiently formed, as shown in the preceding sub-section. The $V_{\pm}(\Delta E_{\text{CM}} \text{ Max})$ and $V_{\pm}(\Delta E_{\text{CM}}=0)$ limits (black and blue dashed lines) have been calculated for the process $\text{O}^+(\text{}^2\text{D or } \text{}^2\text{P}) + \text{CD}_4 \rightarrow \text{CD}_3^+ + \text{OD}$. It is more difficult to calculate the limit for the dissociative charge transfer channel $\text{CD}_3^+ + \text{D} + \text{O}$, because we have three bodies on the product side. However, if a two-step process is assumed, i.e. a charge transfer leading to CD_4^{+*} followed by the decomposition of CD_4^+ into $\text{CD}_3^+ + \text{D}$, then the CD_3^+ velocities for the $\Delta E_{\text{CM}}=0$ limit are expected to be at the same position as the CD_4^+ velocities for the charge transfer $\Delta E_{\text{CM}}=0$ limit, with some additional broadening due to the $\text{CD}_4^{+*} \rightarrow \text{CD}_3^+ + \text{D}$ fragmentation. This is why the $V_{\pm}(\Delta E_{\text{CM}}=0)$ limits for the charge transfer process $\text{O}^+(\text{}^2\text{D or } \text{}^2\text{P}) + \text{CD}_4 \rightarrow \text{CD}_4^+ + \text{O}$ remain good references for the dissociative charge transfer channel too and have been added to Figure 10 (red dashed line). We can see that the measured velocity distributions for CD_3^+ from the $\text{O}^+(\text{}^2\text{D or } \text{}^2\text{P}) + \text{CD}_4$ reactions are essentially in the backward direction indicating that almost thermal ions are produced in the laboratory frame (very close from the red dashed line lower limit) as for the

charge transfer products in the $O^+(^4S) + CD_4$ reaction. This is not surprising if CD_3^+ ions stem from the dissociative charge transfer process.

In principle, the production of CD_3^+ ions could also be accounted for by the hydride transfer leading to $CD_3^+ + OD$ which is an exothermic channel (O3), even from the $O^+(^4S) + CD_4$ ground state entrance channel. As the CD_3^+ velocity distributions are much closer to the $V_-(\Delta E_{CM}=0)$ limit (lower blue dashed line) than the $V_{\pm}(\Delta E_{CM} \text{ Max})$ limits (black dashed line), this means that, if the hydride transfer occurs, the kinetic energy exchanged between parent and product ions would be a very small fraction of the available energy as for direct processes occurring at large distances. However, although strongly forward or backward scattering have already been observed for D or D^- transfers, one might expect that more momentum transfer occurs in such transfers than for a charge transfer because of the much lighter mass of the electron relative to D^- . As CD_4^+ and CD_3^+ velocity distributions are very close, this could be an indication that CD_3^+ production stems from the dissociative charge transfer process rather than from the hydride transfer.

DISCUSSION

In the previous section, the dependence of the reaction cross sections and velocity distributions to the excitation of O^+ parent ions from 4S ground state to 2D and 2P metastable states and to collision energy has been described from an experimental point of view. In this section, we will discuss the nature of the channels accounting for the production of the observed ions on the basis of the experimental results presented above,^{19, 33-38} calculations of potential energy surfaces³⁸⁻⁴⁰ and trajectory simulations.³⁹ We mainly aim at elucidating the reaction mechanisms and the nature of the major oxygenated compounds that are expected to be produced by the reaction of

$O^+(^4S, ^2D, ^2P)$ ions with methane, in particular to get some clues on the role of oxygen on Titan's chemistry. Note also that, unless stated otherwise, no distinction has been made between normal species and ^{18}O - or D-substituted species, in the following discussion.

The production of H_xCO^+ ions, with the formation of a new C-O bond, has been observed and well characterized at low and high collision energies by Levandier et al³⁸ in their study of the $O^+(^4S) + CH_4$ reaction. H_3CO^+ , H_2CO^+ and HCO^+ ions originate from the loss of H and H_2 from the reaction complex. As these processes are very exothermic (see Equations O8, O9 and O10 and Figure 1), further dissociation of H_3CO^+ and H_2CO^+ is energetically possible leading to $HCO^+ + H_2 + H$. This explains why, among all the H_xCO^+ ionic species, the production of HCO^+ dominates, being however a much less efficient process, at any collision energies, than the charge transfer. At large collision energies, according to classical trajectory simulations by Sun et al,³⁹ the opacity function calculated for HCO^+/H_2CO^+ formation decreases rapidly with the impact parameter, thus leading to small cross sections and restricting the reaction to direct impacts of the oxygen atom with the carbon atom. This is consistent, as discussed by Levandier et al,³⁸ with a high conversion of the available energy into internal energy and then to the recoil energy of the leaving H and H_2 leading to HCO^+ ions with very low kinetic energy in the CM frame, as observed.³⁸ For low collision energy, the low efficiency of H_xCO^+ production relative to the charge transfer is more surprising for this exoergic processes and could be due to a spin-forbidden mechanism coupling the quartet entrance channel ($O^+(^4S) + CH_4(X^1A_1)$) to a doublet surface.³⁸ For the reaction of $O^+(^2D, ^2P)$, we have shown that the H_xCO^+ production remains a minor channel, probably because it also competes with more direct mechanisms occurring at larger impact parameters leading to CH_3^+ ions, especially at large collision energies. At low collision energy, as the entrance channels are now doublet surfaces ($O^+(^2D, ^2P) + CH_4(X^1A_1)$), it

is interesting to note that no quartet to doublet transitions is required to reach the H_xCO^+ product surfaces and that spin-forbidden mechanisms cannot be invoked to account for the low efficiency of this process, unlike for the $\text{O}^+(^4\text{S})$ case.

H_2O^+ production, through the process (O7), is also mediated by a long lived complex for the reaction of $\text{O}^+(^4\text{S})$,³⁸ as corroborated by the $(E_{\text{CM}})^{-0.47}$ dependence of the cross section and the product velocity distributions centered on the center of mass velocity, V_{CM} , observed by Levandier.³⁸ It is a more efficient process than H_xCO^+ production, constituting an appreciable fraction (about 30 % in our work and 20% in Levandier et al) of the main channel, the charge transfer leading to CH_4^+ , but only at low collision energy. The H_2O^+ production indeed decreases drastically with collision energy. For the reaction of $\text{O}^+(^2\text{D}, ^2\text{P})$ ions, no H_2O^+ production has been measured, within our sensitivity limit, even at low collision energy. This seems to indicate that adding electronic energy also reduces considerably the efficiency of the process. It could also be possible that the couplings between the entrance surfaces and the intermediate complex leading to H_2O^+ production are much weaker for the doublet metastable states than for the quartet ground state.

OH^+ production has been observed on a much larger range of collision energies for the reaction of $\text{O}^+(^4\text{S})$,^{35, 38} but it is nevertheless a minor process only decreasing slowly with collision energy as confirmed by classical trajectory simulations.³⁹ On the contrary to H_2O^+ and H_xCO^+ production, it does not stem from the decomposition of a long lived complex but mainly from a spectator stripping mechanism where the H atom is transferred (O4 channel) without much exchange of momentum leading to forward scattering of OH^+ ions as shown in the experimental and theoretical studies.^{35, 38-39} Its production does not seem to be promoted by O^+ parent ion excitation to ^2D or ^2P states, as shown in this work. In the study by Ottinger et al, for an ion-

source discharge conditions ($U_A = 90$ V) at which metastable states represent about 30-35 % of the total O^+ population, OH^+ ions are observed (see Figure 2 in their paper³⁵), but in a same amount, within the $\pm 20\%$ experimental uncertainties, as for the source conditions ($U_A = 40$ V) at which only pure $O^+(^4S)$ ($\approx 97\%$) are produced. Using the equality between the cross sections, σ_{MIX} and σ_{4S} , measured for mixed (70% 4S + 30% $^2D+^2P$) and pure ground state (4S) population of O^+ and the $\pm 20\%$ error bar limits, they have deduced that, σ_{2D2P} , the cross section for the reaction of the pure $^2D+^2P$ metastable states, would be between $1.67.\sigma_{4S}$ and $0.33.\sigma_{4S}$, i.e. 67% higher or lower than the ground state cross section. This leads to an estimation of σ_{2D2P} , at 2 eV collision energy, between 0.2 and 1 Å² confirming that the OH^+ production is a minor channel, even for the reaction of the metastable states.

All the ions formed in the $O^+(^4S, ^2D, ^2P)$ reactions and discussed so far, are minor products except H_2O^+ but only at low collision energy and for the reaction of ground state O^+ . The two major products for the reactions of $O^+(^4S)$ and $O^+(^2D, ^2P)$ with methane are in fact CH_4^+ and CH_3^+ ions respectively.

For CH_4^+ , the situation is clear, it can only be formed by the charge transfer (O1). The slow decrease of the cross sections with collision energy associated with a product velocity distribution strongly backscattered at thermal velocities in the laboratory frame observed in this work and other studies,^{35, 38-39} are consistent with a direct exothermic process occurring at long distances.

With O^+ excitation to 2D or 2P states, the entrance channels being 3.3 and 5 eV higher in energy than for the 4S ground-state reaction, the charge transfer is strongly reduced in favor of CH_3^+ production (see Figure 5-8), and also of CH_2^+ production even though its ratio to CH_3^+ is about

15% only for the $O^+(^2D)$ reaction (see Figure 9, Panel (b)), as if new very competing channels would be now accessible. As shown in Figure 1, the two dissociative charge transfer channels (O3) and (O6), leading to $CH_3^+ + H + O$ and $CH_2^+ + H_2 + O$ are possible candidates. However, CH_3^+ and CH_2^+ can also be formed by channels (O2) and (O5), leading to $CH_3^+ + OH$ by hydride transfer and $CH_2^+ + H_2O$. It would be surprising though that the (O2) and (O5) processes would become much more efficient upon excitation of O^+ to 2D and 2P metastable states as they are already exothermic for the reaction of $O^+(^4S)$.

For the $CH_2^+ + H_2O$ channel (O5), we would expect that it is mediated by the complex dissociation, in a similar way as for the $H_2O^+ + CH_2$ channel (O7). However, the observed increase of the cross section with collision energy for $O^+(^4S)$ reaction does not advocate for the formation of CH_2^+ ions by the exothermic process (O5), except at low collision energy where it is very inefficient, but rather by channel (O6) which is endothermic by 1.54 eV. For $O^+(^2D, ^2P)$ reactions, the cross section for CH_2^+ production is highly enhanced, but quite constant with collision energy, and the hypothesis of CH_2^+ formation through the $CH_2^+ + H_2O$ channel is also rather improbable. On the contrary, the hypothesis of the formation of CH_2^+ through the dissociative charge transfer channel (O6), which is exothermic for the excited state reaction, is compatible with such a collision energy dependence, similar to the one observed for the charge transfer channel (O1) in the reaction of $O^+(^4S)$.

The situation is comparable for the formation of CH_3^+ ions. They can be produced, for the reaction of $O^+(^4S)$, either by the very exothermic ($\Delta H = -3.69$ eV) hydride transfer (O2), or by the endothermic ($\Delta H = +0.71$ eV) dissociative charge transfer (O3), and the measured cross section also increases with collision energy (see Figures 5 and 9). The analysis of product

velocity distributions has been discussed very carefully by Levandier et al.³⁸ It is a complex problem since, in the $O^+(^4S) + CD_4$ reaction, OD^+ ions are produced at the same mass as CD_3^+ ions. Nevertheless, by recording TOFs at nominal or lower values of the RF voltages of the octopoles, they manage to identify on the velocity distributions two contributions from OD^+ ions, one in the forward direction and one in the backward direction, but close to the V_{CM} velocity, and one contribution for CD_3^+ ions, more strongly scattered in the backward direction, though not as much as for the CH_4^+ charge transfer product because some conversion of kinetic energy to internal energy is required (see for instance the comparison of Figures 3b and 4a at $E_{CM} = 2$ eV³⁸). The latter component dominates with increasing collision energy and may be associated with dissociative charge transfer or hydride transfer as both mechanisms are known to produce backscattered products.⁶¹⁻⁶³ It is interesting to note that the asymptote leading to the hydride transfer channel when the two products are in their electronic ground state, $CH_3^+(X^1A_1) + OH(X^2\Pi)$, is a doublet surface, which can be coupled to the entrance quartet surface, $O^+(^4S) + CD_4(X^1A_1)$, by a spin-forbidden mechanism only. This was used as a possible explanation for the low efficiency of the hydride transfer at low collision energy, at which the dissociative charge transfer (O3) is not yet energetically possible. However, as originally proposed by Ottinger et al.,³⁵ and later discussed by Sun et al.,³⁹ the hydride transfer channel can be reached without any quartet to doublet transition, if the first excited triplet state of CH_3^+ is formed instead. Taking the methyl radical vertical ionization to the first triplet state, $^3E'$, measured by Dyke et al.,⁶⁴ the production of $CH_3^+(^3E') + OH(X^2\Pi)$ channel is endothermic by 1.23 eV, however adiabatic ionization values should be preferred here for the calculation. The calculated energy for $CH_3^+(^3E') + OH(X^2\Pi)$ by Sun et al is 0.22 eV at the PM3 level but -0.01 eV at the MP2 level.³⁹ Very recent high level CASSCF/MRCI calculations by Delsaut and Liévin⁶⁵ show

that this state undergoes Jahn-Teller distortions which places the minimum of the first triplet state, $\text{CH}_3^+(\text{}^3\text{A}'')$ in C_s symmetry, at about 3.52 eV above the $\text{CH}_3^+(\text{X}^1\text{A}_1')$ ground state, and hence the formation of $\text{CH}_3^+(\text{}^3\text{A}'') + \text{OH}(\text{X}^2\Pi)$ channel is exothermic by about 0.17 eV and could be energetically accessed from the $\text{O}^+(\text{}^4\text{S}) + \text{CH}_4$ entrance channel already. As a consequence, the low efficiency of the hydride transfer at low collision energy cannot be accounted for by a spin-forbidden mechanism only, and has to be related to a preferred coupling of the entrance channel to the charge transfer exit channel, which is overwhelmingly produced. The observed rise of the cross section for CH_3^+ production with increasing collision energy is an indication that the dissociative charge transfer (O3), which is endothermic by about 0.7 eV, is more efficient than the hydride transfer to form these ions, although the hydride transfer cannot be completely excluded, as already proposed by Levandier et al.³⁸

For the $\text{O}^+(\text{}^2\text{D}, \text{}^2\text{P})$ reactions, the parent ion excitation also promotes the CH_3^+ production but much more efficiently than the collision energy. The measured velocity distributions (see Figure 10) have very strongly backward scattered components that are characteristic of either dissociative charge transfer or hydride transfer. The dissociative and non-dissociative charge transfer of rare gas cations on methane is well-documented and efficient near resonant charge transfers are observed.⁶⁶⁻⁷³ For charge transfer processes involving reactions of atomic A^+ ions with molecule targets such as methane, two criteria are usually important for a good coupling between charge transfer states, the good overlap between $\text{CH}_4(\text{v}=0)$ and $\text{CH}_4^+(\text{v}^+)$ vibrational wavefunctions, and the energy difference, ΔE , between the two states, $\text{A}^{+*} + \text{CH}_4(\text{v}=0)$ and $\text{CH}_4^+(\text{v}^+) + \text{A}^*$. For the case of rare gas cations and methane, ΔE values of ± 0.5 eV are generally observed. In the photoionization of methane,⁷⁴⁻⁷⁸ the CH_4^+ ion yield increases only slowly above threshold, indicating that the Franck-Condon factors (FCF), (i.e. the squared vibrational wave

function overlap, between the vibrational ground state of CH_4 and vibrational states, v^+ , of CH_4^+) are small for the low v^+ level and increases only gradually. There are good overlaps however for excess energies between 0.5 and 3 eV above the ionization threshold.⁷⁸ For the charge transfer process, this means that if the $\text{A}^{+*} + \text{CH}_4(v=0)$ entrance channel is too close to the $\text{CH}_4^+(v^+=0) + \text{A}^*$ limit, there are no way to find a sufficiently excited level, v^+ , for which both criteria are satisfied. On the contrary, if $\text{A}^{+*} + \text{CH}_4(v=0)$ is well above the $\text{CH}_4^+(v^+=0) + \text{A}^*$ limit, there are CH_4^+ vibrational excited states, $\text{CH}_4^+(v^+)$, for which the $\text{A}^{+*} + \text{CH}_4(v=0)$ initial state can be nearly resonant with the final $\text{CH}_4^+(v^+) + \text{A}^*$ state and, as the same time, the FC factor between $\text{CH}_4(v=0)$ and $\text{CH}_4^+(v^+)$ is large. In that case, the electronic energy of A^{+*} is converted to vibrational energy of CH_4^+ without transfer of too much kinetic energy between reactant and products in a near-resonant process.

For the $\text{O}^+ + \text{CH}_4$ reaction, one can see in Figure 1 that, for each of the O^+ initial state, ^4S , ^2D and ^2P , there is at least one final state of the O atom among ^3P , ^1D and ^1S , for which $\text{O}^{+*} + \text{CH}_4(v=0)$ is in the good energy window above the $\text{CH}_4^+(v^+=0) + \text{O}^*$ limits to allow for an efficient charge transfer as the first step of the collision. Note also that for all these combinations of O^{+*} and O^* states, the recombination is a spin-allowed process, as it corresponds to transitions from doublet to either triplet or singlet states, or from quartet to triplet states. This is an important point to make for the reactions of atomic ions, as this property could have direct consequences on their product branching ratio. Indeed, for the nitrogen case, the $\text{N}^+(^3\text{P})$ ground state can recombine to the $\text{N}(^4\text{S})$ ground state and the $\text{N}(^2\text{D}, ^2\text{P})$ excited states, however the $\text{N}^+(^1\text{D})$ metastable state can only recombine to the $\text{N}(^2\text{D}, ^2\text{P})$ excited states. It was shown that this could explain why, in the $\text{N}^+ + \text{CH}_4$ reaction, the dissociative charge transfer channel surprisingly decreases in favor of the non-dissociative charge transfer upon N^+ excitation from ^3P ground state to the metastable ^1D

state.^{56, 79-80} For the oxygen case, as there is no spin-forbidden transition for the recombination between the states of interest, it is expected that the dissociative charge transfer channel would increase with the additional energy brought by O^+ excitation. This is consistent with the observations made for the $O^+(^2D, ^2P) + CH_4$ reactions. As visible in Figure 1 for these reactions, the intermediate vibrationally excited CH_4^+ ions have sufficient energy to dissociate into $CH_3^+ + H$. For the $O^+(^4S) + CH_4$ reaction, it is not the case, as the intermediate step, $CH_4^+ + O(^3P)$, is below the first dissociative charge transfer limit, and additional collision energy is needed to pass the threshold. However, large conversion of kinetic energy to internal energy (CH_4^+ vibrational energy) is required for that, and this kind of process is not as efficient as the electronic to internal energy conversion invoked for the $O^+(^2D, ^2P) + CH_4$ reactions. This is probably the reason why, as already mentioned before, the branching ratios between CD_4^+ and CD_3^+ products measured in the “TPEPICO” mode for the $O^+(^4S) + CD_4$ reaction at $E_{CM} = 5$ eV and for the $O^+(^2P) + CD_4$ reaction at $E_{CM} = 0.2$ eV, i.e. with the same total initial energy (about 5 eV), but with two very opposite repartitions between O^+ internal energy and collision energy, are very different (see last point in Figure 5 and first point in Figure 7). Very efficient non-dissociative and dissociative charge transfer corresponding to exothermic channels have also been observed in the reactions of $O^+(^4S)$ ions with ethane, propane and n-butane producing ions at near thermal velocities too.⁴⁵ It is interesting to note that, an increase with collision energy of several product ions is observed, that can be accounted for by endothermic dissociative charge transfer processes,⁴⁵ in a similar way as for the $CH_3^+ + H + O$ products in the $O^+(^4S) + CH_4$ reaction. The mechanism that we have described here for CH_3^+ production initiated by charge transfer, and eventually followed by the dissociation of CH_4^+ ions, has the advantage over the hydride transfer mechanism to naturally account for the concomitant increase of CH_3^+ ions and decrease of CH_4^+ ions with O^+ excitation

from 4S to 2D or 2P states. Moreover, as we don't see much difference in Figure 10, within experimental uncertainty, between the backward scattered velocity distributions of CD_3^+ ions and CD_4^+ ions produced by the $O^+(^2D, ^2P) + CD_4$ and $O^+(^4S) + CD_4$ reactions respectively, we believe that the dissociative charge transfer is the most probable mechanism to account for the methyl cation production.

Coming back to the $CH_2^+ : CH_3^+ : CH_4^+$ branching ratio, we should note, as already mentioned, that the CH_2^+ production could possibly stem from the dissociative charge transfer (O6) for the $O^+(^2D, ^2P)$ reactions. Actually, if we follow the same mechanism as the one proposed for the CH_3^+ production, which goes through the $CH_4^+(v^+) + O(^3P, ^1D, ^1S)$ intermediate steps for the $O^+(^2D, ^2P)$ reactions, it is expected that the $CH_2^+ + H_2 + O(^3P, ^1D, ^1S)$ channel competes with the $CH_3^+ + H + O(^3P, ^1D, ^1S)$ one with the O excitation being the same through all the process as it cannot change after the first charge transfer step. Note that if the near resonant charge transfer of O^+ on methane occurs for ΔE values of ± 0.5 eV as for rare gases, or eventually larger, then the non-dissociative charge transfer channel leading to $CH_4^+ + O(^1S)$ can be observed for the $O^+(^2D) + CH_4$ reaction (for positive values of ΔE to reach a zone of non-zero FCF) and also for the $O^+(^2P) + CH_4$ reaction (for negative values of ΔE to stay below the $CH_3^+ + H + O(^1S)$ dissociation limit). This could explain the non-dissociated CH_4^+ products observed in the two $O^+(^2D, ^2P)$ reactions. Whereas the $CH_2^+ : CH_3^+$ branching ratio should be given by the CH_4^+ breakdown diagram as a function of its internal excitation,⁸¹⁻⁸² which is known to favor the $CH_3^+ + H$ products over several eV above the first dissociation threshold (the crossing point for equal CH_2^+ and CH_3^+ production occurring at about 7 eV only above threshold).⁸² The shape of the breakdown diagram can be explained by the energetics, as the $CH_2^+ + H$ channel is about 0.84 eV higher than the $CH_3^+ + H$ channel, but is also related to the nature of the transition state over

which the dissociation occurs for each channel. One can see on Figure 1 that, for the $O^+(^2D) + CH_4$ reaction, it is difficult to reach the $CH_2^+ + H_2 + O(^1D)$ channel and impossible to reach the $CH_2^+ + H_2 + O(^1S)$ channel, and for the $O^+(^2P) + CH_4$ reaction, it is impossible to reach the $CH_2^+ + H_2 + O(^1S)$ channel. Whereas for the $CH_3^+ + H + O$ production, one has an additional solution for each of the $O^+(^2D)$ and $O^+(^2P)$ reaction showing, at least qualitatively, that the CH_2^+ / CH_3^+ ratio is expected to be small as measured (about 0.15) for the $O^+(^2D)$ reaction (see Figure 9, Panel (b)). We have not tried to predict more quantitatively this ratio as several paths are available for CH_3^+ production, which complicates the task.

We have not tried either to model the relative efficiency of the $O^+(^2D)$ and $O^+(^2P)$ reactions. As described in the results section, very similar behaviors was found in the two reactions, for the nature of the products, their velocity distributions and the branching ratio between the two main CH_3^+ and CH_4^+ products, with the exception that the measured cross sections are slightly smaller for the $O^+(^2P)$ reaction (see Figures 6-8). In the model that we propose, the first step is the charge transfer. Therefore, the overall efficiency of the reaction, as measured by the yield of the two main products (see Figure 8), is expected to depend on this initial step only. However, it is difficult to quantify the relative efficiency of the charge transfer for the two states, as we know that the couplings between charge transfer states are dependent on small details on the potential energy surfaces, and an estimation of these factors is out of the scope of this work.

CONCLUSION

In the reaction of purely state-selected $O^+(^4S, ^2D, ^2P)$ ions with methane, we have shown that the production of CH_4^+ ions, which is the main channel observed for the reactions of the 4S ground state is greatly reduced in favour of the formation of CH_3^+ ions, and also CH_2^+ ions but in much

smaller amounts, with O^+ excitation to either 2D or 2P metastable state. Whereas the overall reactivity is slightly reduced going from 4S to 2D and to 2P . CH_3^+ production is also increased with collision energy in the reaction of $O^+(^4S)$, however much less efficiently than with O^+ excitation. Rather flat dependences with collision energy are observed otherwise, for the CH_3^+ production in $O^+(^2D, ^2P)$ reactions and the CH_4^+ production in the $O^+(^4S, ^2D, ^2P)$ reactions. These major products are strongly back scattered in all cases, which is characteristic of direct mechanisms occurring at long distances.

All these observations are consistent with a unique mechanism, initiated by an efficient charge transfer process producing CH_4^+ ions and O atoms in a variety of states, which can lead to the production of $CH_3^+ + H + O$ or $CH_2^+ + H_2 + O$ when CH_4^+ ions are produced with sufficient vibrational excitation to dissociate.

As a consequence for the oxygen chemistry in Titan's ionosphere, we believe that for all the $O^+(^4S, ^2D, ^2P)$ reactions, the main oxygenated product is mostly the O atom except for the $O^+(^4S)$ reaction and at low collision energy only for which H_2O^+ ions are also produced in a relatively large proportion (20-30 %) of the main $CH_4^+ + O$ channel. Nevertheless, many other minor channels have been identified by Levandier et al³⁸ for the $O^+(^4S)$ reaction which include OH and OH^+ products stemming from direct hydride or hydrogen transfers, and H_xCO^+ ions where a new CO bond is formed. For the $O^+(^4S, ^2D, ^2P)$ reactions, we have also identified minor productions of HCO^+ ions.

The other point that should be made in the comparison of the O^+ reactions with N_2 and CH_4 is related to the exothermicities of the respective charge transfer reactions, which differ by about 3 eV. First of all, it should be stressed that for collision energies below 1 keV,³¹ efficient O

production for the reaction with N_2 is possible from the $O^+(^2D, ^2P)$ metastable states but not from the $O^+(^4S)$ ground state for which $NO^+ + N$ is mainly formed. Moreover, if no kinetic energy is transformed into internal energy, which is probably the case as such conversion is not very efficient, the $O^+(^2D) + N_2$ charge transfer can only produce $O(^3P)$ state, and the $O^+(^2P) + N_2$ charge transfer can produce $O(^3P)$ and $O(^1D)$ states but not the $O(^1S)$ state. Whereas for the reaction with methane, the $O(^3P)$ state is produced very efficiently by charge transfer from the $O^+(^4S)$ ground state already, and all three $O(^3P, ^1D, ^1S)$ states are possibly formed, though with different probability, by the non-dissociative or dissociative charge transfer from the $O^+(^2D)$ or $O^+(^2P)$ states.

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ABBREVIATIONS

TPEPICO, Threshold PhotoElectron PhotoIon Coincidences; TPES, Threshold PhotoElectron Spectrum; GIB, Guided Ion Beam; SR, Synchrotron Radiation; VUV, vacuum-ultraviolet; CM, center of mass; TOF, Time Of Flight; FCF, Franck-Condon factor; SIFT, selected ion flow tube;

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Insert Table of Contents Graphic and Synopsis Here.

Enceladus and Titan