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State-selected ion-molecule reactions relevant to the chemistry of Titan's ionosphere

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Abstract

To quantify the production of neutral oxygen O atoms from atomic O^+ ions, the reactions of state-selected $O^+(^4S, ^2D, ^2P)$ atomic ions ($^{16}O^+$ and $^{18}O^+$) with methane (CH_4 and CD_4) have been studied. Absolute cross sections for the ionic product formations have been measured as a function of electronic excitation of O^+ and collision energy. With electronic excitation of the O^+ parent ion from the ground state ^4S to the long lived excited states ^2D and ^2P, a reduction of the total cross section and a complete inversion of the branching ratio between the main products (CH_4^+ and CH_3^+) are observed.

1. Introduction

The objectives of this work are derived from the very recent debate on the role of oxygen species in the chemistry of Titan atmosphere [1]. It appears that these species could be initiated by O^+ cations that are injected on Titan from another Saturn satellite, Enceladus, as confirmed by the observation of precipitating O^+ flux by the Cassini Plasma Spectrometer [2]. The charge transfer (CT) of O^+ ions producing neutral O atoms would be the starting point of the chemistry of oxygen in Titan neutral atmosphere. Thus, it appears very important to caracterize as well as possible the reactions of O^+ with the two most abundant neutrals of Titan's atmosphere, N_2 and CH_4. In previous works, the reaction of ground state $O^+(^4S)$ with methane was studied in details by Levandier *et al* as a function of collision energy [3] and the reactions of $O^+(^4S, ^2D, ^2P)$ with N_2 were caracterized by Li *et al* [4].

2. The $O^+(^4S,^2D,^2P) + CH_4$ reaction

2.1 Experiment

The reaction of O^+ atomic ions with methane has been studied on the guided ion beam apparatus, CERISES [5]. To avoid mass overlaps and to discriminate against secondary reactions, the three isotopically labeled reactions $^{16}O^+ + CH_4$, $^{16}O^+ + CD_4$ and $^{18}O^+ + CH_4$ have been considered. Absolute reaction cross sections have been measured at selected collision energies for the reaction of O^+ in its ground state $O^+(^4S)$ and first two excited metastable states $O^+(^2D)$ and $O^+(^2P)$ which have very long lifetimes ($\tau(^2D)$ = 1.6-9.1 h and $\tau(^2P)$ = 4.9-6.3 s).

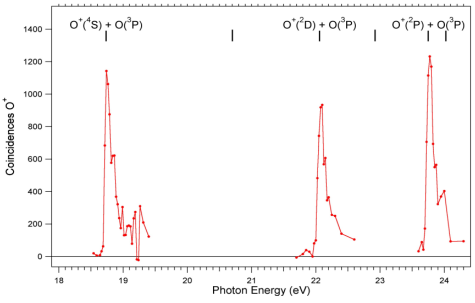

Figure 1: Production of state-selected $O^+(^4S, ^2D, ^2P)$ cations in coincidence with threshold photoelectrons (TPEPICO) by dissociative photoionisation of O_2 with VUV synchrotron radiation.

As shown on Fig. 1, pure state selection of O^+ cations produced by dissociative photoionisation of O_2 has been achieved by using a double threshold technique [5], in which O^+ ions with no recoil kinetic energy were extracted from the source in coincidence with threshold photoelectrons. The experiment is done with VUV radiation in the 18-25 eV range delivered by the DESIRS beamline at the french synchrotron SOLEIL and takes advantage of the 8-bunch operating mode of SOLEIL, in which the interval between two bunches of photons is 148 ns.

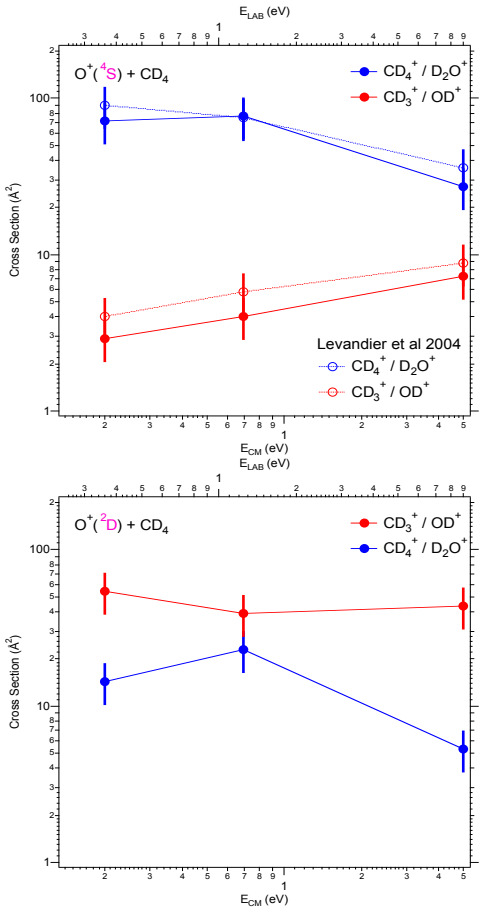

Figure 2: Cross sections for the production of CD_4^+ and CD_3^+ in the reaction of $^{16}O^+(^4S$ and $^2D)$ with CD_4 as a function of collision energy

2.2 Results

For the reactions of $O^+(^4S)$ and $O^+(^2D)$ with CD_4, the measured absolute cross sections are given on Fig. 2 as a function of collision energy, for the production of the two main products CD_4^+ and CD_3^+. Isotope labeling has allowed us to show that D_2O^+ and OD^+, which have the same nominal m/z as CD_4^+ and CD_3^+ (20 and 18 resp.) are minor products even when O^+ is excited. As visible on Fig. 2, we observe a moderate reduction of the total cross section with excitation of O^+ to the ^2D state, but a complete inversion of the branching ratio between the two products, in favor of the CD_3^+ product. This is also true for the O^+ excitation to the ^2P state. We are currently analysing the product velocities to find if the CH_3^+ products are associated with the formation of OH or O + H, which would be very different for the oxygen chemistry. We have now to integrate these new data in a model, as was done for the reaction $N^+(^3P, ^1D) + CH_4$ [6].

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