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Effect of the Vibrational Excitation of CH_3^+ cations on their reactivity with CH_4

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Synopsis The VUV photoionisation of CH_3 radicals formed in a beam by pyrolysis of CH_3NO_2 precursors is used to produce CH_3^+ cations and control their vibrational excitation. The reactivity of CH_3^+ cations with methane is then studied on a Guided Ion Beam setup as a function of both collision energy and CH_3^+ internal energy.

The methyl carbocation is a reactive species which has been detected in a lot of gaseous environments fed by high energy sources such as the interstellar medium, planetary ionospheres as well as laboratory plasmas for methane conversion into higher hydrocarbons for instance. His reactivity with several hydrocarbons is well-known for the ground state whereas only few data about the reactivity of excited CH_3^+ ions are available in the literature although excited species are common in planetary atmospheres and plasmas.

Here, we report on experiments where CH_3^+ ions are generated via direct photoionization of CH_3^{\bullet} methyl radicals, formed in a supersonic beam by pyrolysis of CH_3NO_2 , thus allowing the production of CH_3^+ with a controlled degree of internal excitation when the photon energy is tuned between 9.8 and 12.5 eV on the DESIRS VUV beamline [1] at the French synchrotron SOLEIL.

In a first experiment, the CH_3^+ cation's excitation distribution is measured for each photon energy by the PEPICO (Photoelectron Photoion Coincidence) method using the DELICIOUS III spectrometer [2,3] of the SAPHIRS experiment. In this experiment, we collect all the photoelectrons and measure their kinetic energy in order to derive the distribution of internal energy of the parent ion CH_3^+ by the following equation: $h\nu - \text{IP} = E_c(e^-) + E_{\text{int}}(\text{CH}_3^+)$. We found that, regardless on the photon energy, a ground state population of CH_3^+ is produced and that, by increasing the photon energy, an additional population of very excited CH_3^+ ion is formed.

In the second experiment, CH_3^{\bullet} radicals are formed by the same pyrolysis source which was recently adapted on the Guided Ion Beam setup, CERISES [4], devoted to the study of ion-molecule reactions. VUV photoionization of the CH_3^{\bullet} radicals is used to produce the CH_3^+ cations which are then mass selected and guided to a reaction cell where they react with methane.

Absolute reaction cross-sections have been measured for the $\text{CH}_3^+ + \text{CH}_4$ and $\text{CH}_3^+ + \text{CD}_4$ systems as a function of both collision energy (0.1 – 4 eV) and photon energy. Reaction dynamics and its dependence on the CH_3^+ parent ion vibrational excitation will be discussed.

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