

## 41. — THE ROTATIONAL PREDISSOCIATION OF THE CH<sub>4</sub><sup>+</sup> ION

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Owing to the suggested astrophysical importance of the CH<sub>4</sub><sup>+</sup> and CH<sub>3</sub><sup>+</sup> ions [1-4] in connection with the chemistry of interstellar medium, we wish to report at this meeting on the population mechanism and the monomolecular decay of CH<sub>4</sub><sup>+</sup> ions as obtained by electron impact on methane at low pressure. The decay mechanism as observed in our laboratories with a lifetime in the 10<sup>-6</sup> second range, is described by mechanism (1):



This long lifetime decaying process was observed as a « metastable transition » in the first field free region of a double focussing Nier-Johnson type mass spectrometer using electron impact on CH<sub>4</sub>. In this instrument the ion source temperature was of about 450 K and the FWHM of the metastable peak enables us to determine a total kinetic energy excess on the decay products of about 5 meV. It was also shown in our laboratory [5] that this process was not populated through a Franck-Condon transition between the CH<sub>4</sub> molecule and the dissociation asymptote giving rise to CH<sub>3</sub><sup>+</sup> ions (14.25 eV). In fact the dissociation continuum related to process (1) is populated through the decay of a superexcited state of CH<sub>4</sub> lying near 16 eV. In such a case, the CH<sub>3</sub><sup>+</sup> ion appears with a vibrational excitation energy of about 1.75 eV which is not exceedingly high if one takes into account the fact that the process CH<sub>3</sub><sup>+</sup> → CH<sub>2</sub><sup>+</sup> + H requires at least 5.38 eV in excess with respect to the threshold energy for the appearance of CH<sub>3</sub><sup>+</sup>. Furthermore informations about mechanism (1) are resulting from:

(i) an experiment reported by SMITH and FUTRELL [6] which shows that the lower lifetime limit for CH<sub>4</sub><sup>+</sup> dissociation through process (1) lies around 10<sup>-3</sup> sec.;

(ii) the report made by SOLKA *et al.* [7] of a positive effect on the kinetic energy released in the metastable transition by heating the methane before its ionization between 400 K and 550 K.

These results imply that a possible mechanism for the decay of CH<sub>4</sub><sup>+</sup> into fragments could be found in the tunneling of H(D) through a rotational

barrier near the threshold energy of process (1). In such a case, any substantial increase of the  $\text{CH}_4$  temperature before ionization would correspond to an increase in the total width of the metastable peak, corresponding to a larger kinetic energy release.

In our more recent experiments, which we will describe in detail in a full paper<sup>[8]</sup>, the  $\text{CH}_4$  temperature was extended up to about 1500 K using a monsplasmatron ion source coupled with the tandem mass spectrometer previously used to detect the position in energy of quasi-bound states in diatomic hydride ions<sup>[9,10,11]</sup>. These experiments have shown that if the total width of the metastable peak was, as expected, extended up to 60 meV for  $\text{CH}_4^+$  and to 20 meV for  $\text{CD}_4^+$  by sampling of  $\text{CH}_4^+$  and  $\text{CD}_4^+$  ions in the  $10^{-6}$  second range, the occurrence of many quasi-bound states was observed in these metastable peaks by the modulation of the kinetic energy distribution by discrete energy states occurring respectively for  $\text{CH}_4^+$  at 0 – 1.9 – 6.0 – 25.7 – 60.5 meV and for  $\text{CD}_4^+$  at 0 – 0.6 – 2.9 – 6.7 – 12.6 and 20.9 meV.

It follows from the presently reported results that the  $10^{-6}$  second lifetime component for the decay of  $\text{CH}_4^+$  and  $\text{CD}_4^+$  by mechanism (1) is due to a rotational predissociation of these ions. In our mind, our results are the first experimental evidence of a tunneling mechanism for the decomposition of a rovibrationally excited polyatomic molecule and also for the lack of randomization of the excitation energy in  $\text{CH}_4^+(\text{CD}_4^+)$  ions prior to their monomolecular decay into  $\text{CH}_3^+$  and H atom.

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