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Experimental and theoretical study of the reaction of C_3N^- with acetylene and ethylene

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Synopsis We investigated the reaction of C_3N^- with acetylene and ethylene both through experimental (Guided ion beam mass spectroscopy) as well as theoretical (ab initio calculations). The main experimental results as well as the potential energy surface illustrating possible reaction pathways for the formation of the observed reaction products are presented.

In 2004, the Cassini Plasma spectrometer (CAPS) on board the Cassini spacecraft [1] recorded a multitude of anions in Titan's ionosphere. Unfortunately, CAPS was designed for detection of electrons rather than anions, thus the resolution does not allow the identification of most anions, except CN^- and C_3N^- , which have been assigned with some confidence.

Our goal is to understand if the anion C_3N^- could, by reaction with unsaturated hydrocarbons, form larger negative species and thus serve as a first step in creating large anions in Titan's atmosphere.

Using the Guided Ion Beam Mass Spectrometer apparatus at the University of Trento, we identify the following main channels for the reaction with ethylene:

$$C_3N^- + C_2H_4 \rightarrow \begin{cases} CN^- + C_4H_4 & (1) \\ H_2C_4N^- + CH_2 & (2) \\ HC_4N^- + CH_3 & (3) \end{cases}$$

and the following reaction channels for acetylene:

$$C_3N^- + C_2H_2 \rightarrow \begin{cases} CN^- + C_4H_2 & (4) \\ HC_3N^- + C_2H^- & (5) \\ H_2 + C_4N^- & (6) \end{cases}$$

It is well known, mass spectrometric experiments do not yield any information about the presence of different isomeric structures in the reaction products. Hence theoretical modeling should be performed to assist in the interpretation of the experimental data and to determine the reaction pathways leading to the identified products. We have performed ab initio calculations using the Gaussian [2], $rMP2/6\text{-}311G{+}{+}^{**}$ level of theory. Minima and transition states of the reaction pathways were calculated and their identity confirmed by frequency calculations. Intrinsic reaction coordinate (IRC) calculations were carried out to certify that the transition states connect the correct minimas. The potential energy surface for the reaction with ethylene is shown in Fig. 1, while the one for acetylene will be presented at the conference.

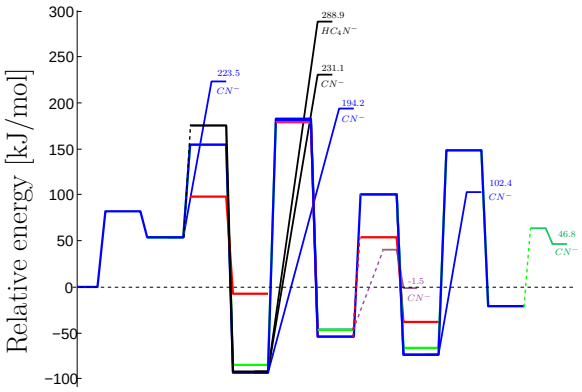

Figure 1. Potential energy surface for reaction C_3N^- with ethylene. Only ion products below 300 kJ/mol are indicated

Calculations indicate that some of the reaction pathways are either endothermic or hindered by high energy barriers, which make them quite unfeasible for Titan's atmosphere. However we see one exothermic product (C_4H_4) that could have great significance for formation of large anions (aerosols) on Titan.

Products from channel (2) is open for energies above 350 kJ/mol, H_2C_4N (anion product formed in channel 2), can contribute to formation of larger $C_{2n}N^-$ anions according [3].

References

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