A theoretical study of formation routes and dimerization of methanimine: implications for the aerosols presence in the upper atmosphere of Titan

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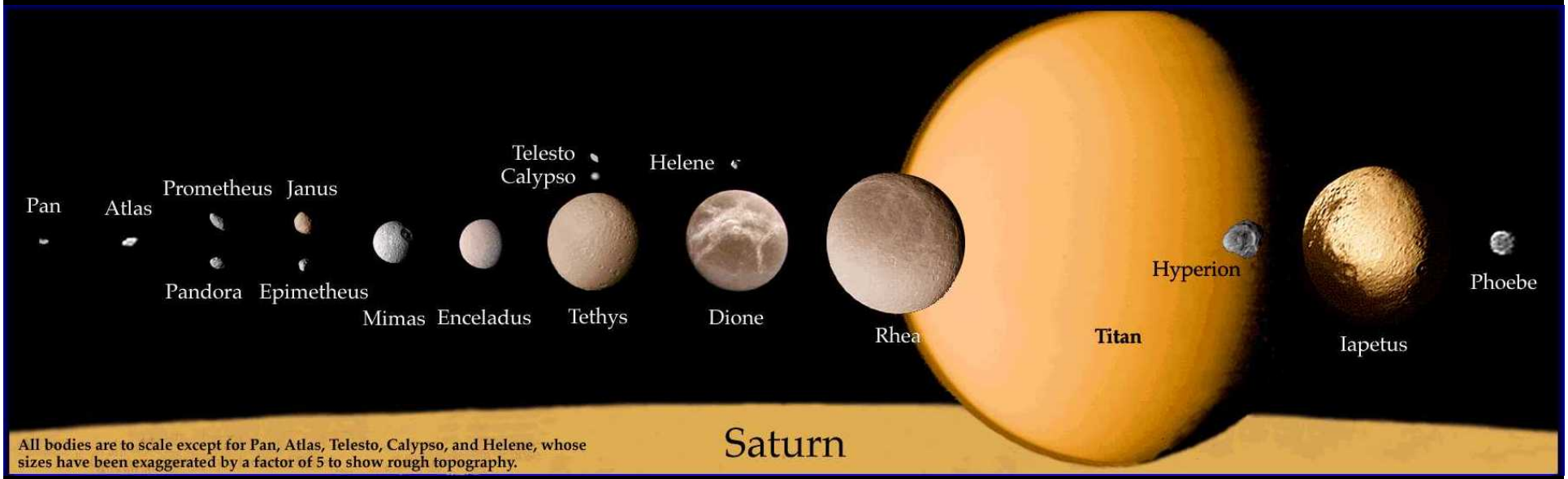
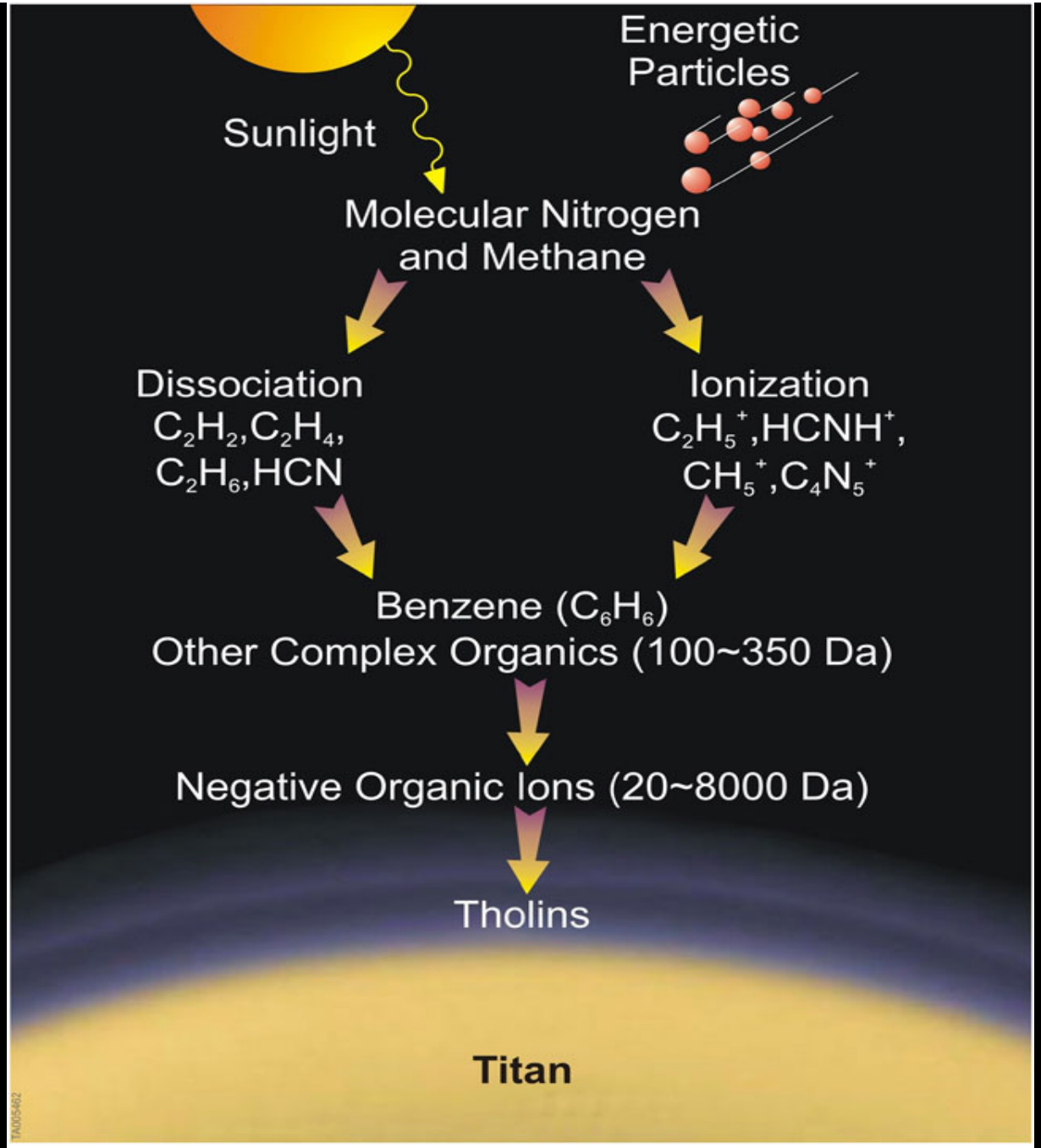
Titan, the massive moon of Saturn



Titan facts

- Surface pressure: 1.6 bar
- Surface temperature: 94 K
- Main constituents of the atmosphere: N_2 (97%), CH_4(2%), H_2, C_2H_6, C_2H_2, C_2H_4, HCN, HCCCN, C_2N_2, … & the **orange haze**

The atmosphere of Titan is believed to be somewhat reminiscent of the primeval atmosphere of Earth



Tholin formation in Titan's upper atmosphere

Nitrogen fixation by photochemistry in the atmosphere of Titan

Molecular nitrogen, the main component of the atmosphere of Titan, is characterized by a strong bond and is difficult to chemically fix in compounds.

The observation of nitriles in trace amounts indicates that some forms of active nitrogen are produced by several processes (e.g. EUV absorption, electron impact) ➲ N, N_2^+, N^+

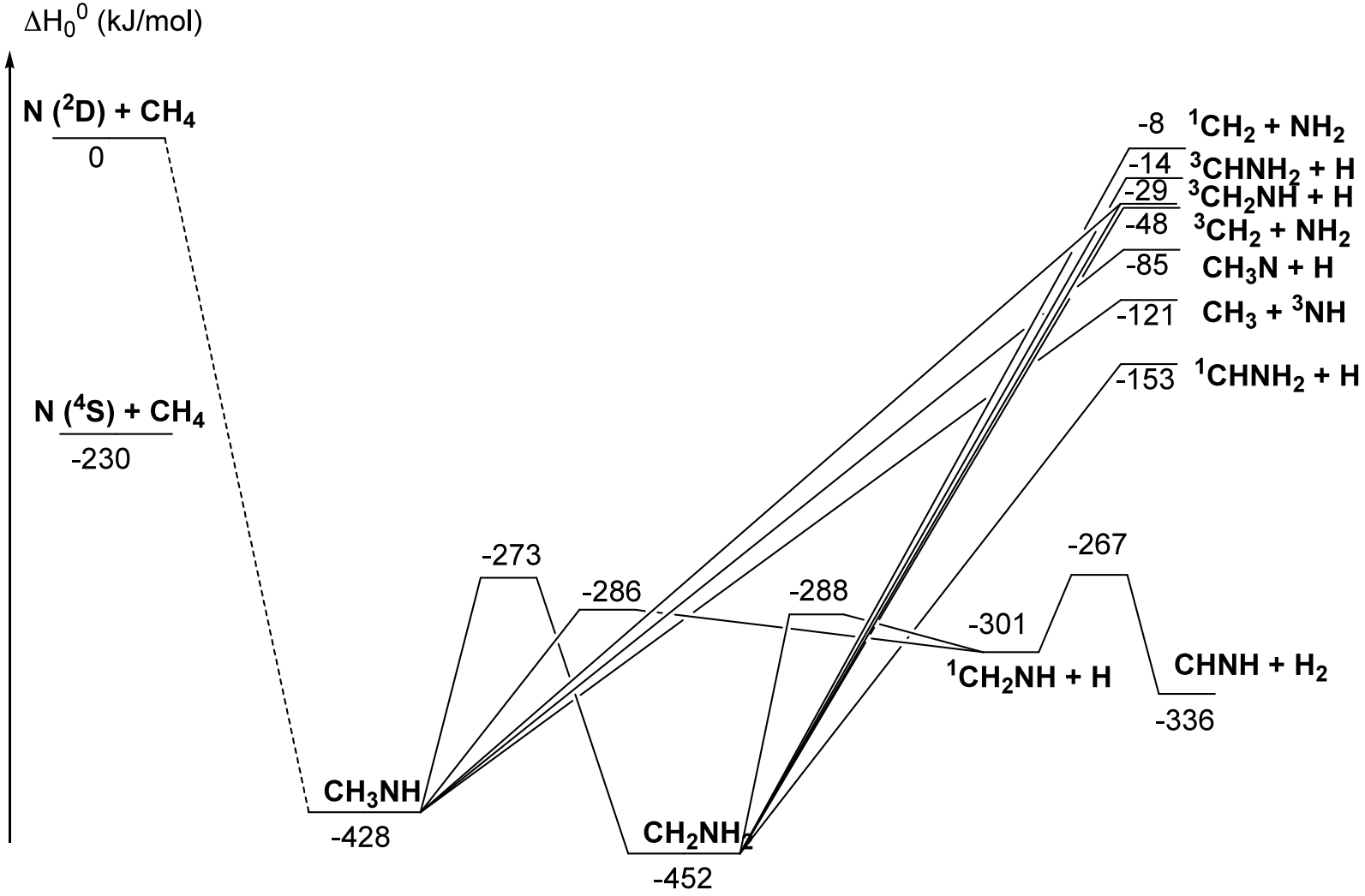
EUV ($60<\lambda<82$ nm) & electron impact induced dissociation, dissociative ionization and N_2^+ dissociative recombination produce $N(^4S)$ and $N(^2D)$ states in similar amounts. The excited ^2D state is metastable with a very long radiative lifetime (~ 48 h).

The generation of atomic nitrogen in the first electronically excited state, ^2D, is extremely relevant in assessing the role of neutral nitrogen chemistry in the atmosphere of Titan because $N(^4S)$ atoms exhibit very low reactivity with closed-shell molecules and the probability of collision with an open-shell radical is small.

Theoretical Calculations

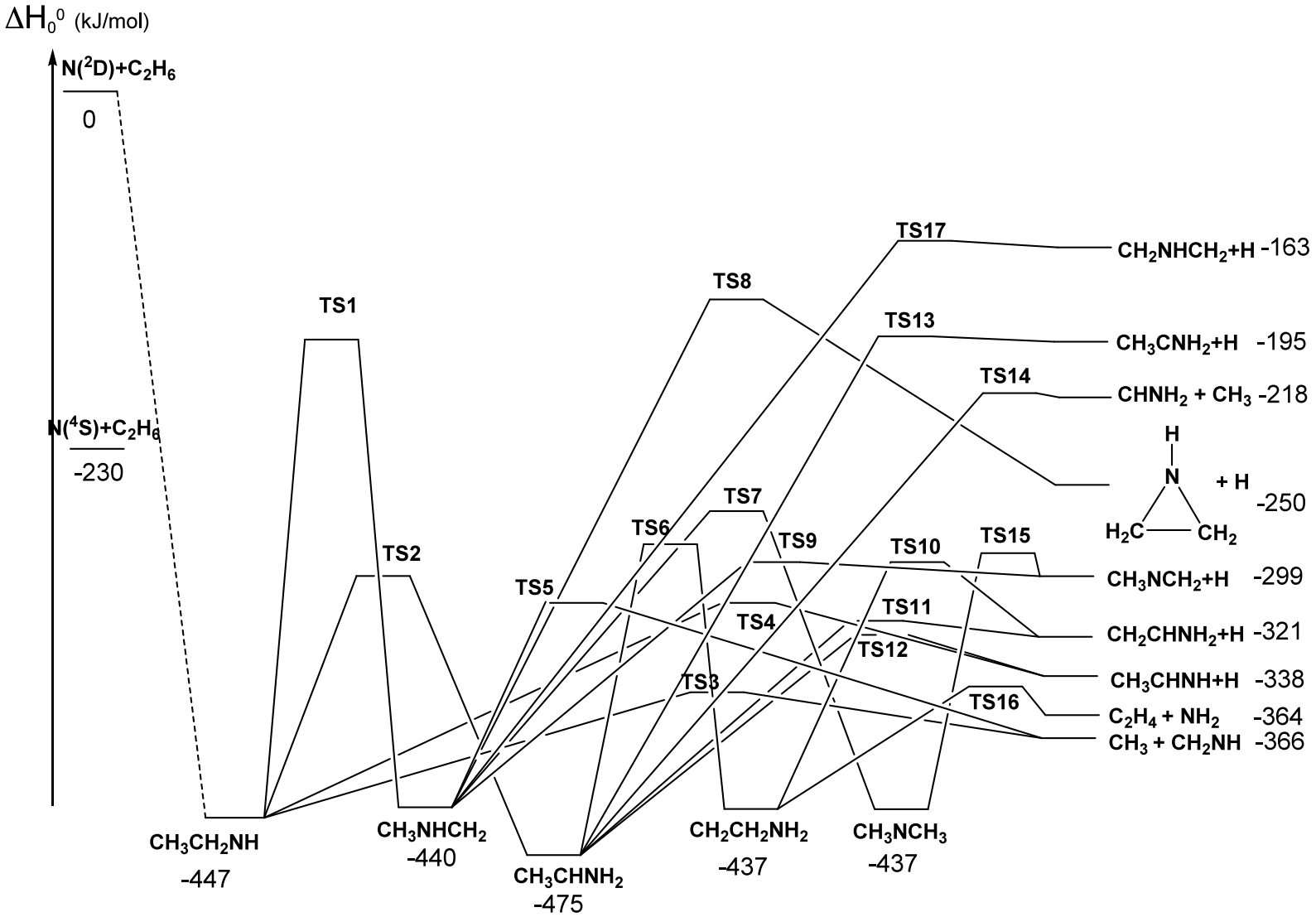
- Density Functional (DFT) calculations using the B3LYP hybrid functional
- Basis sets: triple zeta + polarization + diffuse functions
- Geometry optimizations and localization of transition states at DFT level
- IRC calculations
- CCSD(T) calculations at all the optimized B3LYP geometries
- Thermochemical calculations for selected processes: CBS-Q and W1

The reaction $N(^2D)+CH_4$



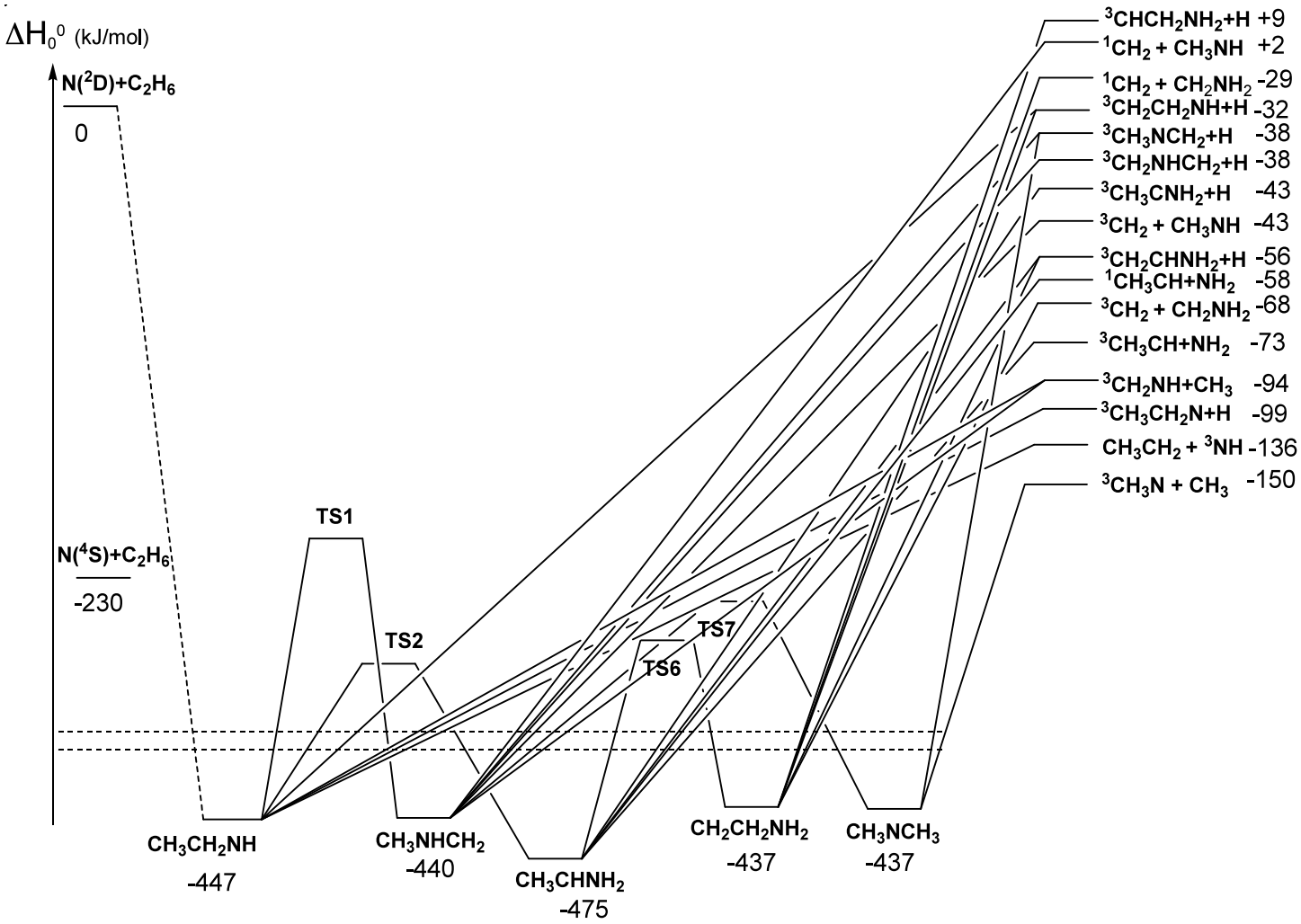
Schematic representation of the $N(^2D) + CH_4$ potential energy surface.
For simplicity only the CCSD(T) relative energies (KJ/mol) are reported

The reaction $N(^2D)+C_2H_6$



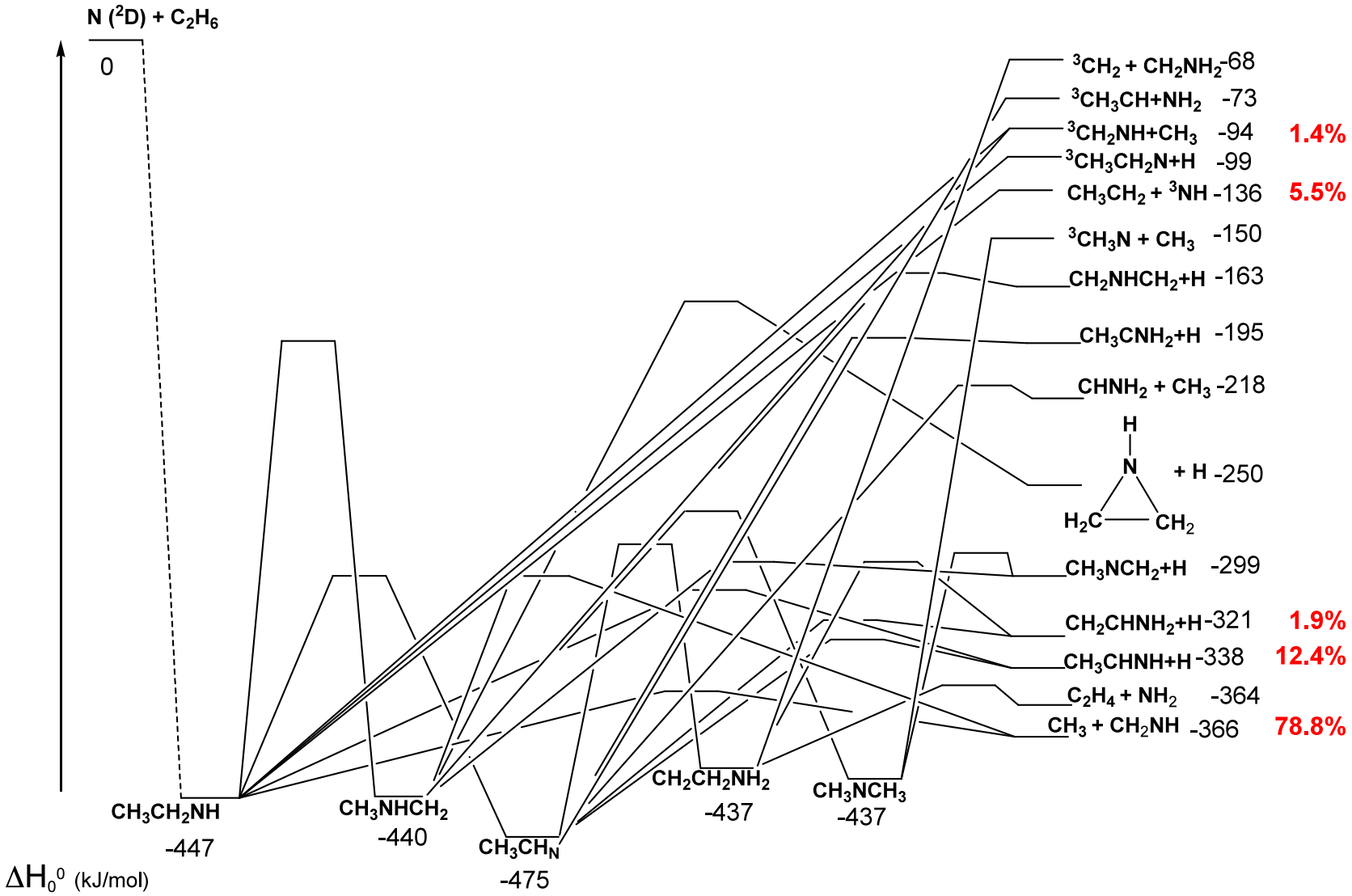
Schematic representation of the $N(^2D)$ + C_2H_6 potential energy surface illustrating the reaction channels which are characterized by an exit barrier. For simplicity only the CCSD(T) relative energies (KJ/mol) are reported

The reaction $N(^2D)+C_2H_6$



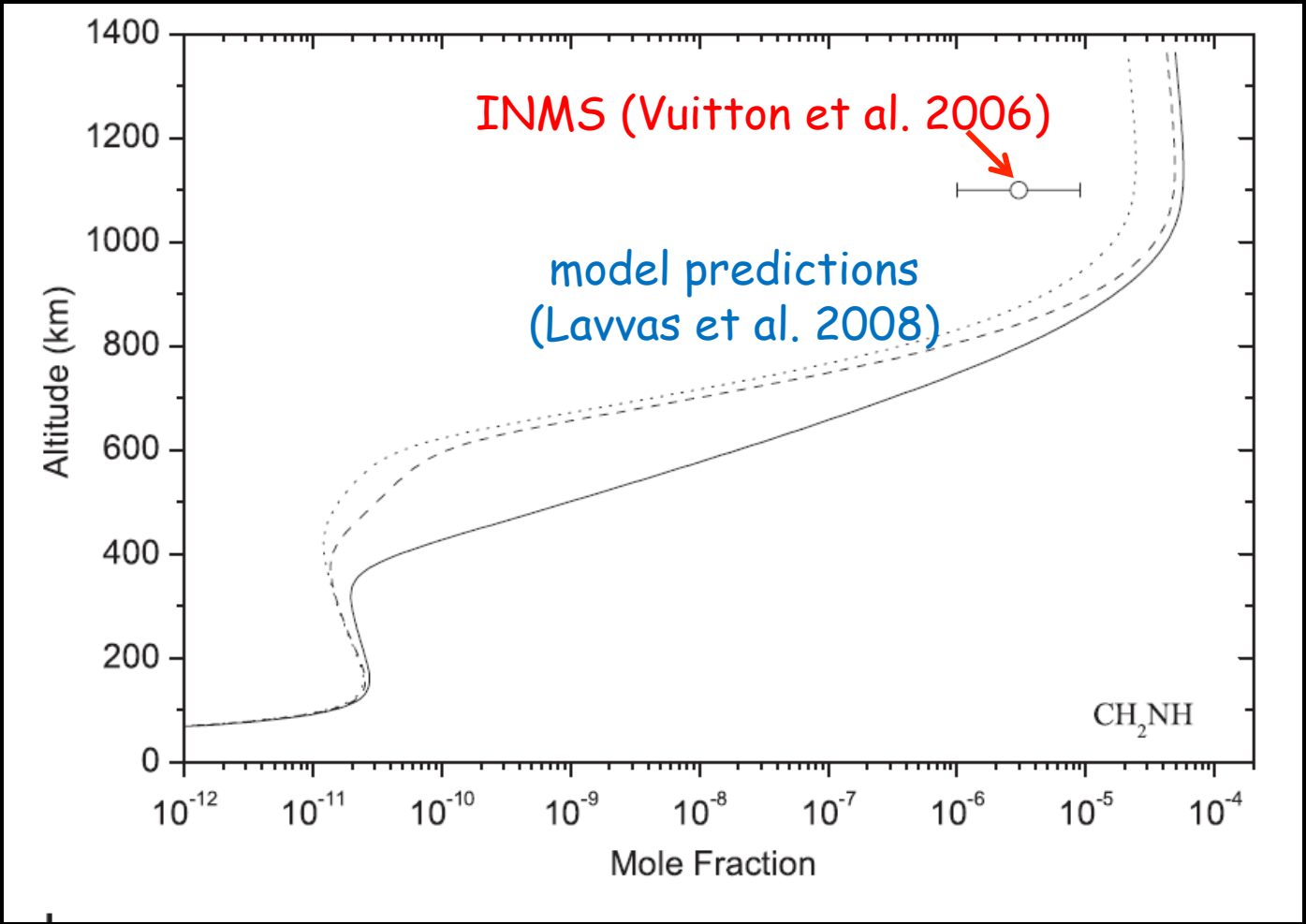
Schematic representation of the $N(^2D) + C_2H_6$ potential energy surface illustrating the reaction channels which are not characterized by an exit barrier. The energy scale has been expanded in the upper part. For simplicity only the CCSD(T) relative energies (KJ/mol) are reported

The reaction $N(^2D)+C_2H_6$



RRKM results

Lavvas et al. (Planet. Space Sci, 2008) have used in their models some of the CH_2NH formation routes and found a quantity of CH_2NH larger than that inferred by Vuitton et al. from the analysis of the INMS data onboard Cassini.

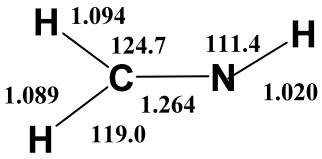


To explain this discrepancy, Lavvas et al. (Planet. Space Sci, 2008) have suggested that, similarly to formaldehyde, CH_2NH can polymerize under the conditions of the atmosphere of Titan. Because of the lack of data on CH_2NH polymerization process, those of formaldehyde have been used.

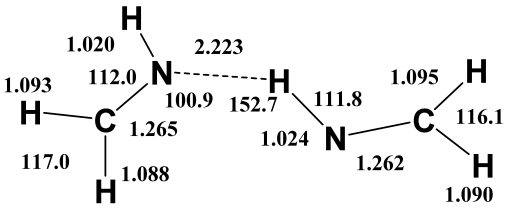
If the polymerization of CH_2NH is confirmed to be extensive, CH_2NH could be one of the basic building block of the nitrogen-rich organic aerosols of Titan.

Because of the lack of data, we have decided to characterize the dimerization of CH_2NH by electronic structure calculations to assess the feasibility of this process under the conditions of Titan.

Dimerization of CH_2NH



CH_2NH



1

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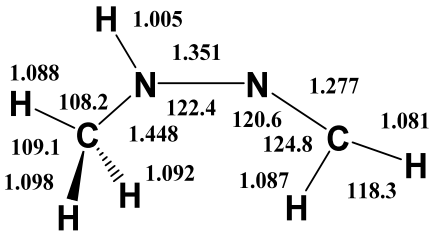

2

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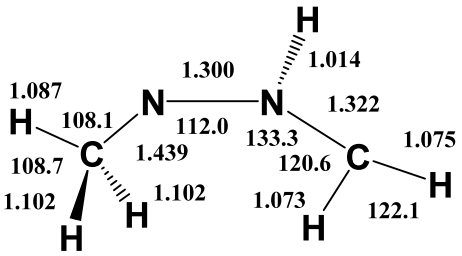

3

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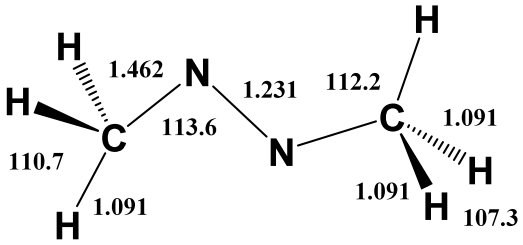

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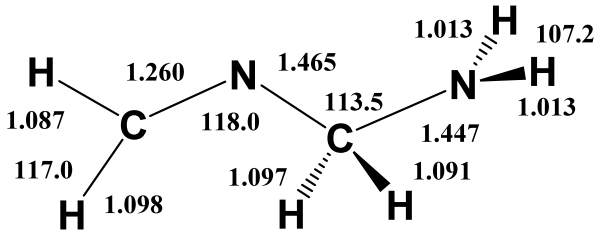

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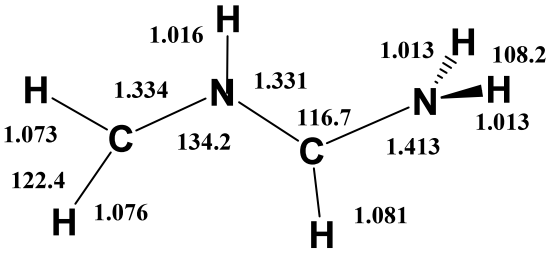
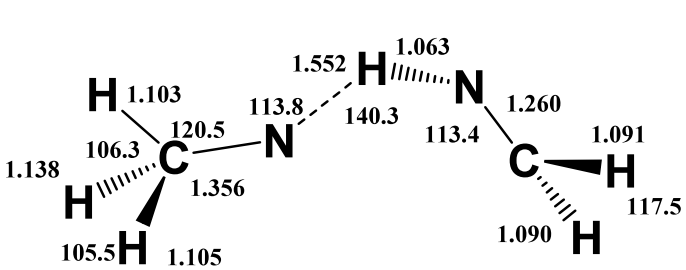


6

63

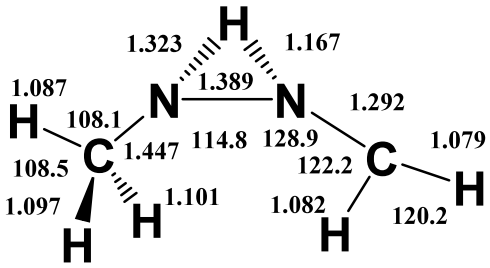
B3LYP optimized geometries (Å and deg) and CCSD(T) relative energies (kJ/mol) with respect to 2 x CH_2NH at 0K of minima localized on the PES of the dimer of CH_2NH.

Dimerization of CH_2NH



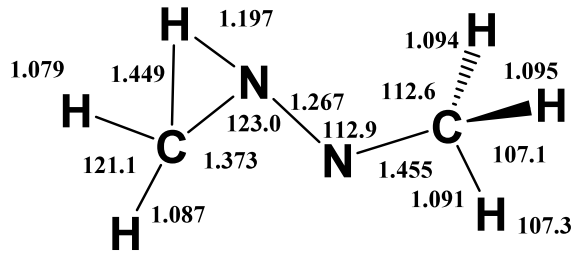
TS 1→2

348



TS 2→3

261



TS 3→4

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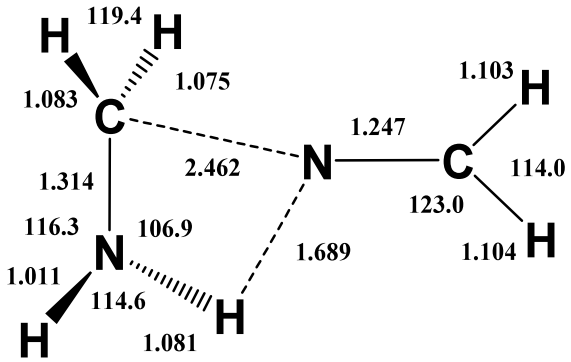

TS 1→5

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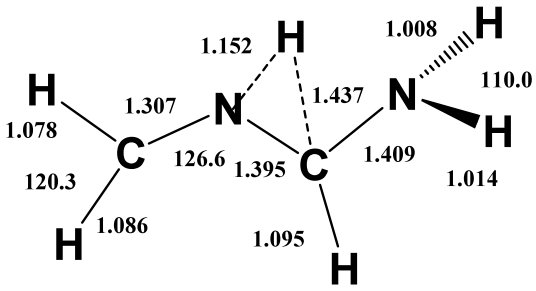
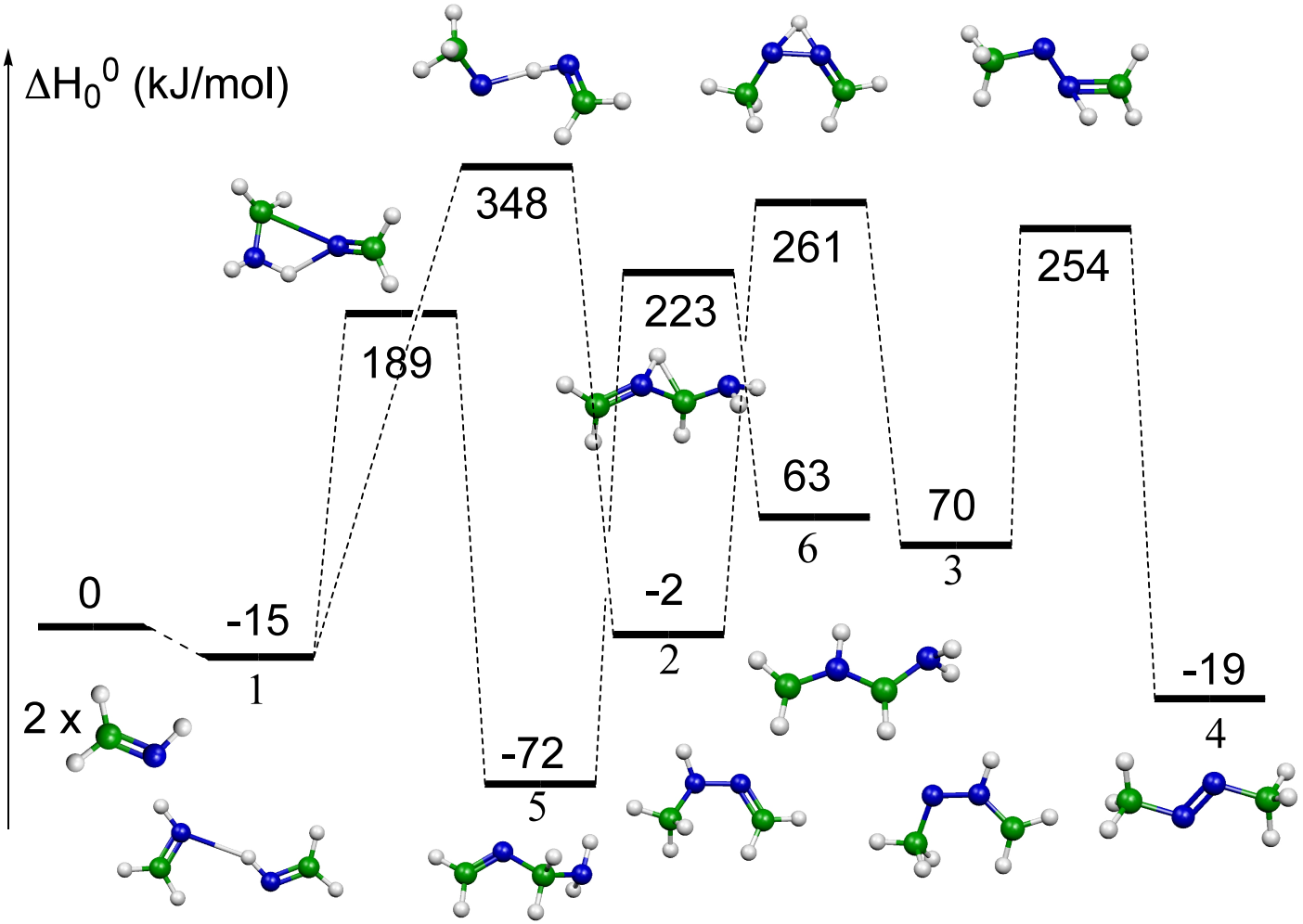


TS 5→6

223

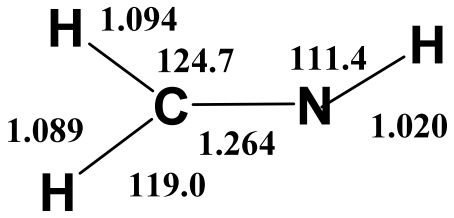
B3LYP optimized geometries (Å and deg) and CCSD(T) relative energies (kJ/mol) with respect to 2 x CH_2NH at 0K of transition states localized on the PES of the dimer of CH_2NH.

Dimerization of Methanimine

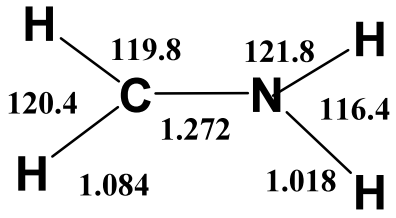


Schematic representation of the potential energy surface for the dimerization of methanimine. For simplicity only the CCSD(T) energies (KJ/mol) relative to 2 x CH_2NH are reported

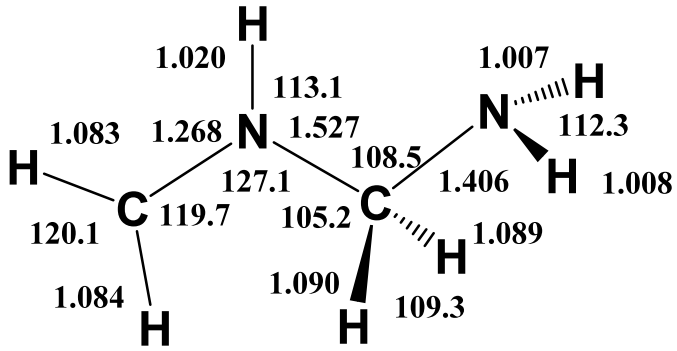
$CH_2NH + CH_2NH_2^+$



CH_2NH



$CH_2NH_2^+$

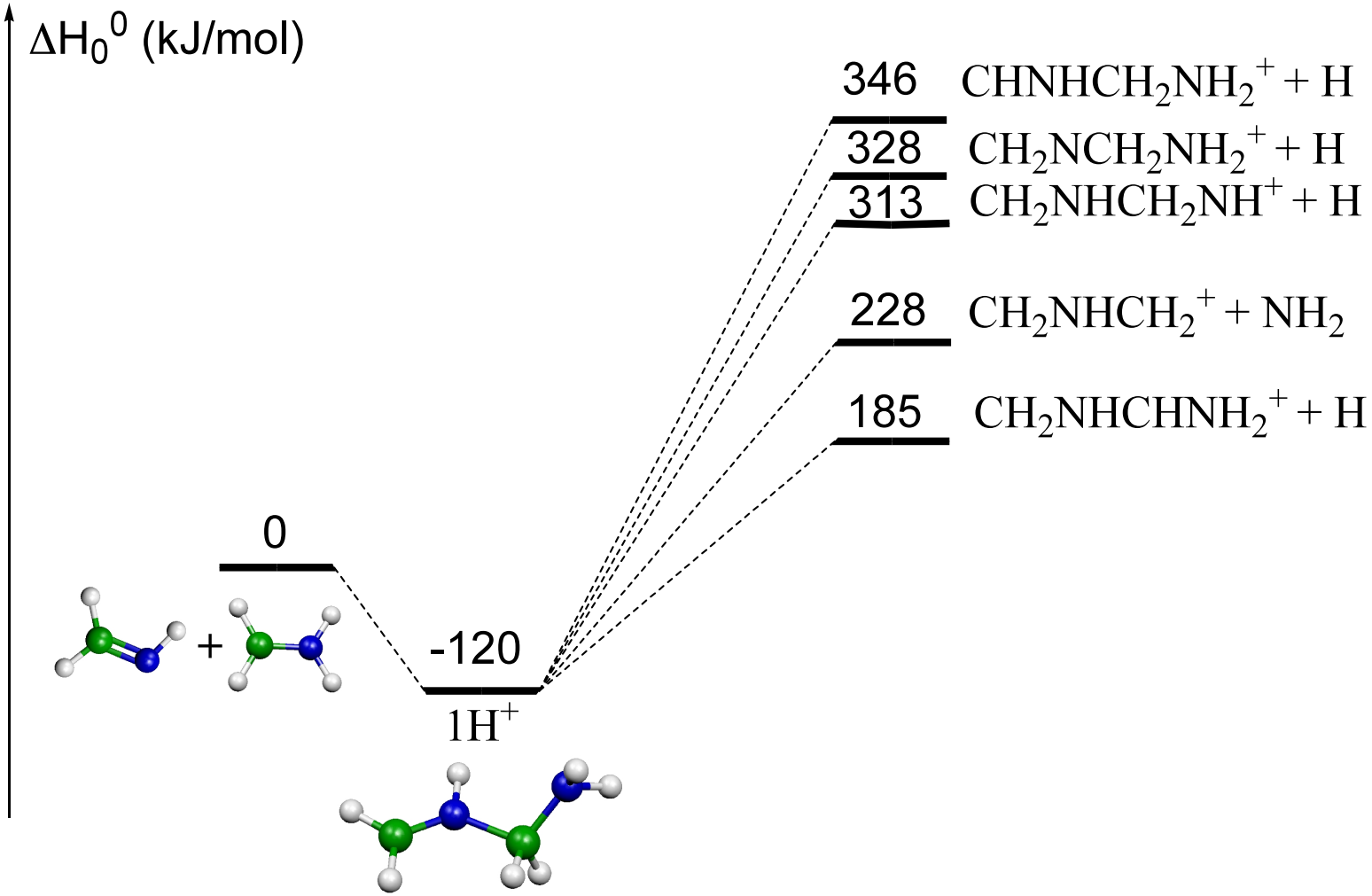


$1H^+$

-120

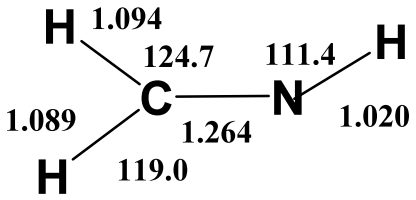
B3LYP optimized geometry (Å and deg) and CCSD(T) relative energy (kJ/mol) with respect to $CH_2NH + CH_2NH_2^+$ at 0K of the protonated dimer species $(CH_2NH)_2H^+$.

Dimerization of Methanimine

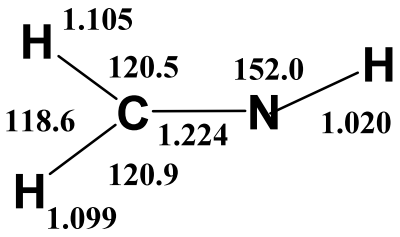


Schematic representation of the potential energy surface for the reaction between CH_2NH and $CH_2NH_2^+$. For simplicity only the CCSD(T) energies (KJ/mol) relative to CH_2NH + $CH_2NH_2^+$ are reported

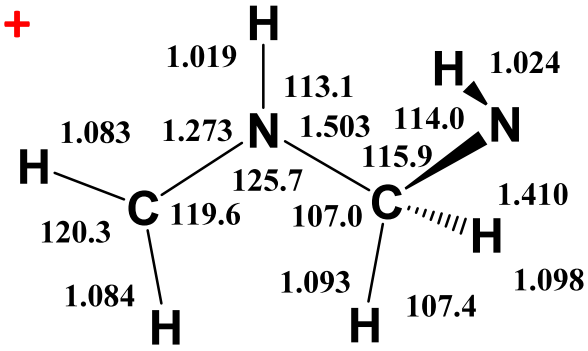
$CH_2NH + CH_2NH^+$



CH_2NH

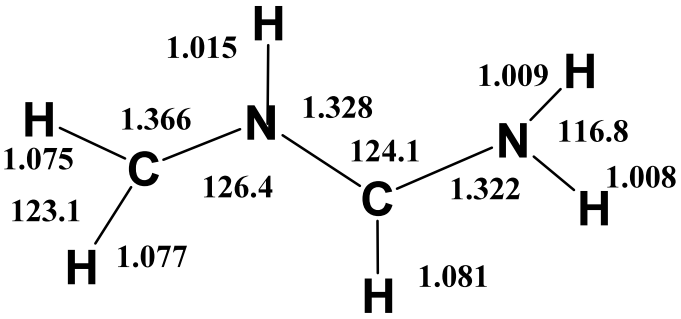


CH_2NH^+



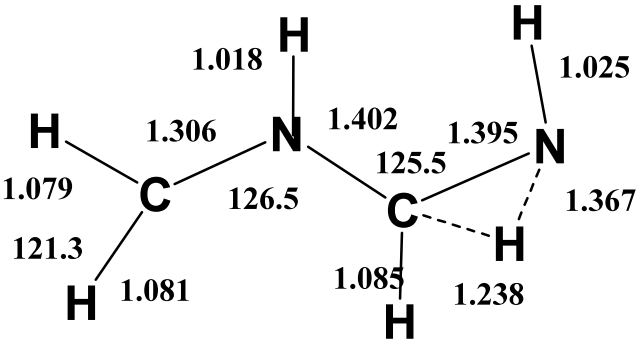
1^+

-167



2^+

-318

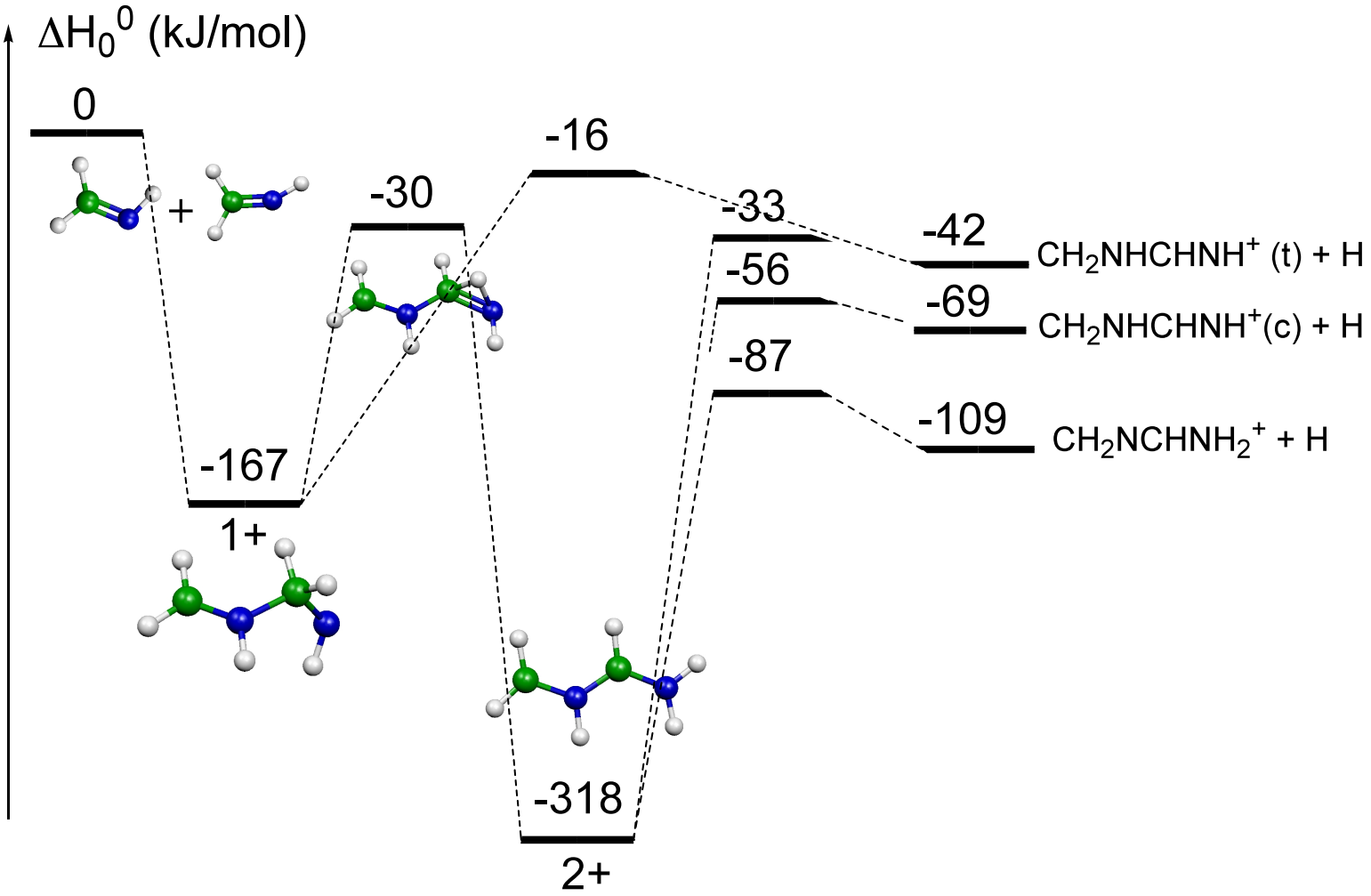


$TS\ 1^+ \longrightarrow 2^+$

-30

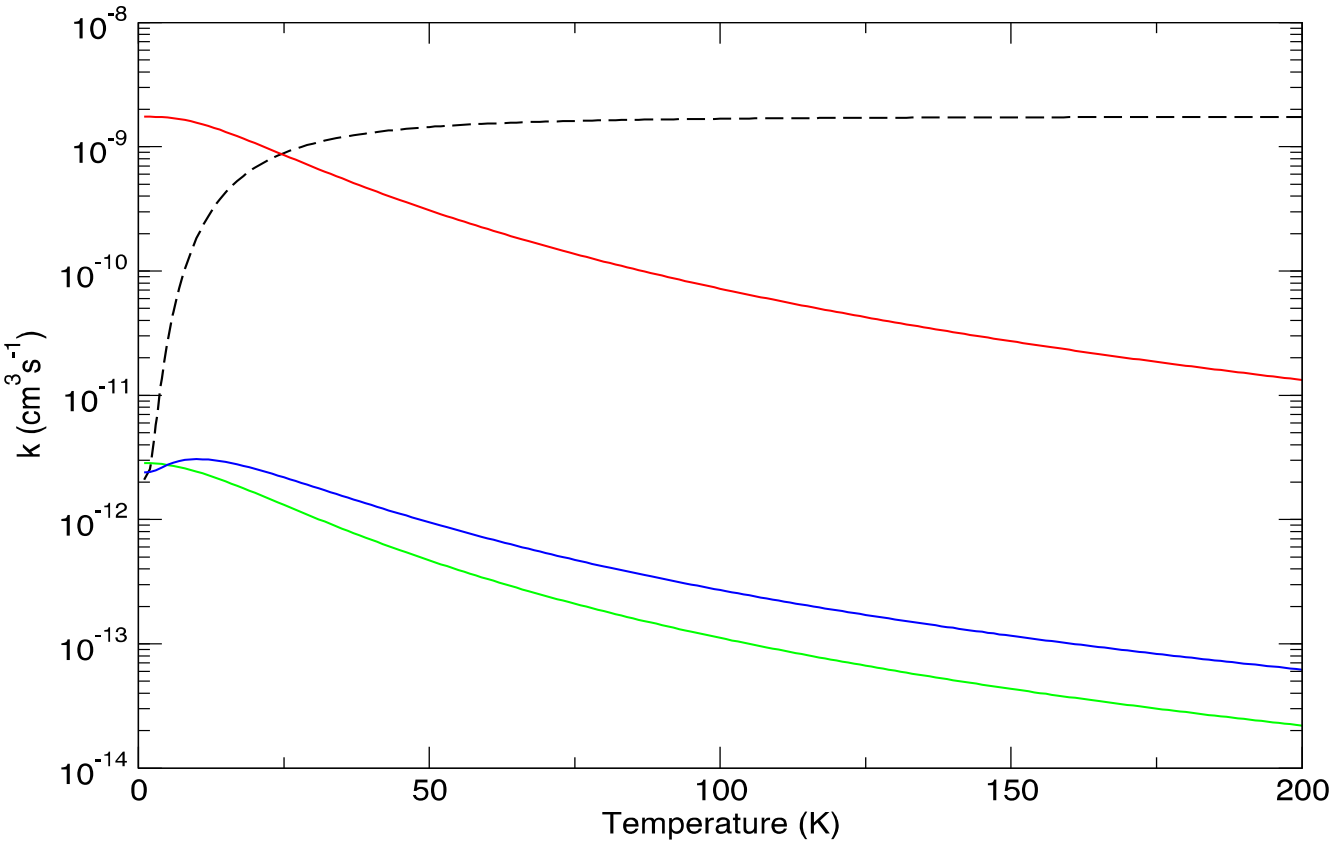
B3LYP optimized geometries (Å and deg) and relative energies (kJ/mol) with respect to $CH_2NH + CH_2NH^+$ at 0K of the stationary points found on the PES of the dimer species $(CH_2NH)_2^+$. CCSD(T) relative energies are reported in parentheses

Dimerization of Methanimine



Schematic representation of the potential energy surface for the reaction between CH_2NH and CH_2NH^+. For simplicity only the CCSD(T) energies (KJ/mol) relative to CH_2NH + CH_2NH^+ are reported

Dimerization of Methanimine



Rate constants as a function of temperature: Back-dissociation (dashed line), $CH_2NCHNH_2^+$ (red), trans $CH_2NHCHNH^+$ (blue), cis $CH_2NHCHNH^+$ (green)

Conclusions

1) Numerous elementary reactions in the upper atmosphere of Titan lead to the formation of methanimine, an important prebiotic molecule

2) Polymerization of methanimine has been invoked to explain the difference between model predictions and Cassini measurements

3) According to our results, dimerization of methanimmine (the first step for polymerization) is a process characterized by very high energy barriers and is difficult to believe it can be important under the conditions of Titan

4) Reactions with ions seems to be more probable loss processes of methanimine