From N(^{2}D) Back to N_2: A Theoretical Investigation of the N(^{2}D) + $CH_2NH \rightarrow N_2$ + CH_3 Reaction and Implications for the Atmospheric Chemistry of Titan

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Abstract. Nitrogen atoms in their first electronically excited state, ^{2}D, are key reactive species in Titan's upper atmosphere, playing a crucial role in the formation of nitrogen-rich organic molecules and shaping the complex organic chemistry of this environment. In this work, we present a theoretical investigation of the reaction N(^{2}D) + $CH_2NH \rightarrow N_2 + CH_3$. Using a combination of density functional theory (DFT) and high-level Coupled-Cluster methods, we explored the stationary points along the minimum energy pathway. Our results indicate that the reaction proceeds without an entrance barrier, with all the internal rearrangements characterized by modest barriers lying well below the reactant energy. Therefore, the reaction is feasible under the conditions of Titan. It remains to be seen whether competitive reaction channels leading to other product sets are open. Given that the actual abundance of CH_2NH is uncertain and may be overestimated in current photochemical models, our findings provide an additional route of methanimine destruction that may help reconcile the predictions of the model with the observed nitrogen chemistry.

Keywords: DFT · Titan's Atmosphere · Potential Energy Surface · Reaction Dynamics

1 Introduction

Methanimine (CH_2NH) is considered a key molecule in prebiotic chemistry [1] due to its potential role as a precursor to glycine being a crucial intermediate in the Strecker synthesis of aminoacetonitrile [2,3]. The presence of methanimine in the upper atmosphere of Titan, the largest moon of Saturn, was established through the analysis of ion spectra obtained by the Cassini Ion Neutral Mass Spectrometer (INMS) which revealed a significant peak at the mass-to-charge ratio of 30 attributed to protonated methanimine [4], with a mole fraction of approximately 1×10^{-5} for the neutral form at an altitude of 1100 km [5]. Since its identification, a number of elementary processes that may

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occur in the thermosphere of Titan have been proposed as possible formation routes and studied using laboratory experiments and/or quantum-chemical calculations [6–9]. Among the considered processes are *i*) reactions between neutral species involving the first excited electronic state of atomic nitrogen (^{2}D) and the abundant CH_4 and C_2H_6 [6,7] and the CH + NH_3 [8] or NH + CH_3/C_2H_5 [10–12] reactions, *ii*) the photodissociation of methylamine, and *iii*) some ion-molecule reactions including electron-ion dissociative recombination of $CH_2NH_2^+$ [9].

Despite its importance, significant discrepancies exist between the predicted and observed mixing ratios of methanimine in Titan's atmosphere, with the predicted abundance consistently overestimating the measured value in all available photochemical models [11,13–15]. This is likely due to limited knowledge of its chemical behavior and, especially, loss mechanisms. Methanimine is a highly reactive molecule that polymerizes readily under terrestrial conditions unless maintained at very low temperatures. This property has led to speculation that its polymerization could contribute to the formation of nitrogen-rich organic aerosols [14,15], which are believed to contribute to Titan's characteristic haze. However, previous studies suggest that the dimerization of neutral methanimine molecules in the gas phase is hindered by significant energy barriers, making it unlikely under the cold conditions of Titan's atmosphere or interstellar space [16]. On the contrary, the processes involving a single molecule of either ionized or protonated methanimine are barrierless and can therefore contribute to the formation of larger ions. In particular, the reaction involving ionized methanimine and neutral methanimine can also be efficient in the very low temperature conditions of Titan, leading to products of general formula $C_2N_2H_5^+$ [17]. The reactivity of methanimine radical cation (H_2CNH^+) and its isomer aminomethylene ($HCNH_2^+$) with the most abundant hydrocarbons of Titan was also investigated [18–20]. Finally, the search for other reactions that can consume methanimine in Titan's atmosphere included the reaction with the CN radical [21], which we know to be abundant, but reactions with C_2H and C_3N are also possible (see [22,23]).

More recently, we have turned our attention to a possible mechanism for N_2 regeneration from the reactions of N(^{2}D) with nitriles (or other nitrogen-containing organic species). This interest stems from the fact that the main channel for the N(^{2}D) + HCN reaction is believed to be the one leading to N_2 + CH [24]. For this reason, we searched for similar channels for the N(^{2}D) reactions with acrylonitrile, acetonitrile, and cyanoacetylene [25–27]. In all cases, the channels leading to N_2 + C_3H_3, CH_2CH/CH_3C, l-C_3H are open, but not competitive. Somewhat surprisingly, we also found that the reaction with pyridine leads to the formation of N_2 and C_5H_5 (cyclopentadienyl), albeit in very modest yield [28]. In this work, we intend to analyze the case of the N(^{2}D) + CH_2NH reaction. The nitrogen atom of methanimine is not involved in a triple bond, as in the case of nitriles. Therefore, it will be very interesting to verify whether the reaction path leading to N_2 + CH_3 is feasible under the conditions of the thermosphere of Titan.

2 Theoretical Methods

The Potential Energy Surface (PES) for the reaction N(^{2}D) + CH_2NH was investigated combining DFT calculations and a more accurate coupled-cluster analysis. As

already done in several cases [26,29–33], geometry optimization and harmonic vibrational frequencies calculations were performed through density functional theory, with the B3LYP functional [34,35] combined with the correlation consistent valence polarized aug-cc-pVTZ basis set [36–38]. Additionally, coupled-cluster [CCSD(T)] [39–41] calculations were performed, with the same basis set, to obtain more accurate values of energy to be used in the PES. All the energy values were corrected using the zero-point energy, evaluated at the DFT level of theory. All calculations were performed using the Gaussan09 software [42] and the visualization of molecular structure was performed using Avogadro [43]. As already noticed in previous investigations [26], single-reference methods, such as B3LYP, provide an unsatisfactory description of the lowest spin excited state. The same results can be obtained including correlation effects (e.g. CCSD(T) calculations). For this reason, the energy of N(^{2}D) was estimated considering the experimental energy difference to N(^{4}S), which corresponds to 230.0 kJ/mol [44]. This value was added to the energy of N(^{4}S) at all levels of the calculation.

3 Results

As a first step of our analysis, a detailed investigation of the entrance channel was performed, in order to identify the presence of a barrier related to the attack of N(^{2}D) to the methanimine molecule. For this reason, a *scan* calculation was carried out at the DFT level, increasing the C-N distance up to 6 Å, with a step of 0.1 Å end evaluating the energy at each step. The resulting plot of the energy as a function of the distance is reported in Fig. 1.

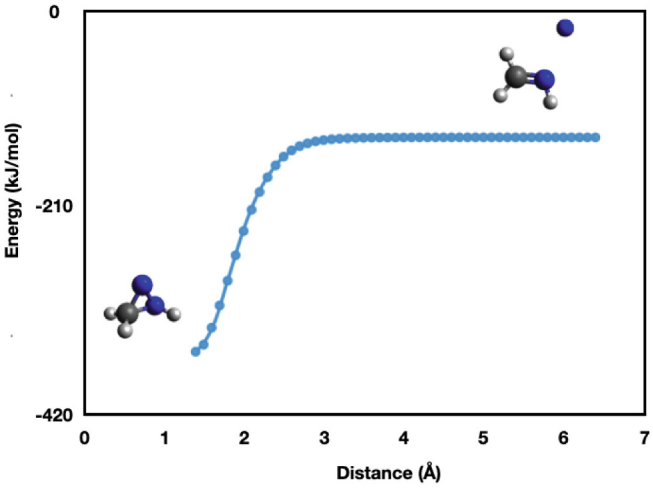

Fig. 1. Energy (kJ/mol) as a function of the C-N distance evaluated for the initial attack of N(^{2}D) to the CH_2NH molecule.

As shown, the energy profile as a function of the intermolecular distance decreases monotonically with decreasing C-N distance, with no evidence of a local maximum along the entrance channel. This behavior indicates the absence of an initial energy barrier, as expected, suggesting that the interaction is barrierless along the explored coordinate.

The potential energy surface is reported in Fig. 2.

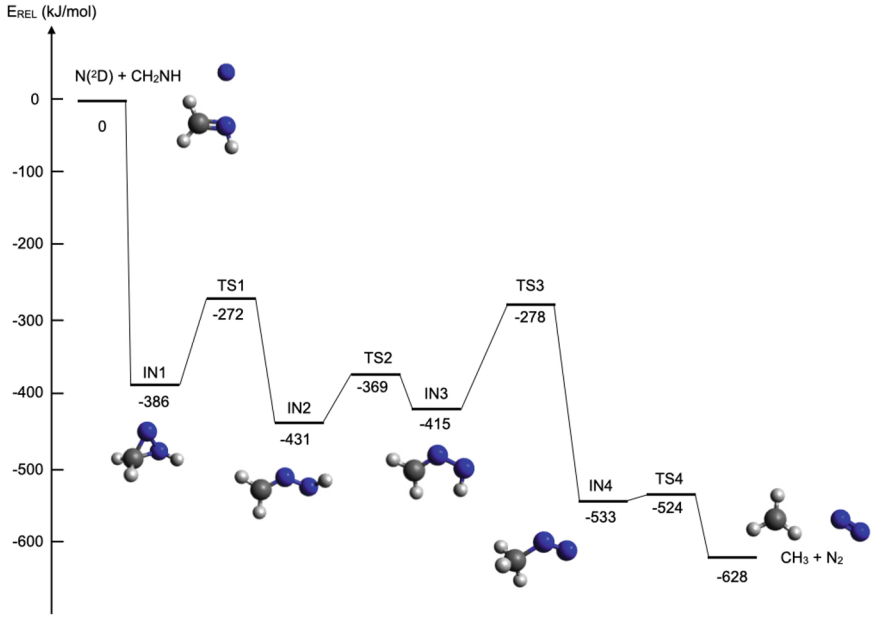

Fig. 2. Schematic representation of the potential energy surface obtained for the $N(^2D)+CH_2NH$ reaction, evaluated at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level of theory.

The first step of the reaction is the barrierless attack of $N(^2D)$ to the C-N double bond of the methanimine molecule, leading to the formation of a stable intermediate (IN1), located 386 kJ/mol below the reactant energy asymptote and characterized by the presence of a three-membered ring in the molecular structure. A barrier of 114 kJ/mol is associated with the C-N bond fission, leading to the formation of a linear intermediate, characterized by the presence of a C-N-N chain. Two different isomers were identified (IN2 and IN3), with a relative energy of −431 and −415 kJ/mol respectively, and connected by a small barrier of 62 kJ/mol (represented by TS2). A C-N hydrogen transfer can be achieved, forming the CH_3NN intermediate (named IN4 in the PES), which

shows a relative energy of −533 kJ/mol. The related transition state (TS3) is located 278 kJ/mol below the energy of the reactants and clearly shows the transfer of an H atom from a nitrogen to the carbon atom of the structure. Finally, a small barrier of 9 kJ/mol is associated to the C-N bond breaking and leads to the formation of molecular nitrogen (N_2) and methyl radical (CH_3). The exothermicity of the products is 628 kJ/mol. In Figs. 3, 4 and 5 are reported the geometries of the stationary points identified in the potential energy surface.

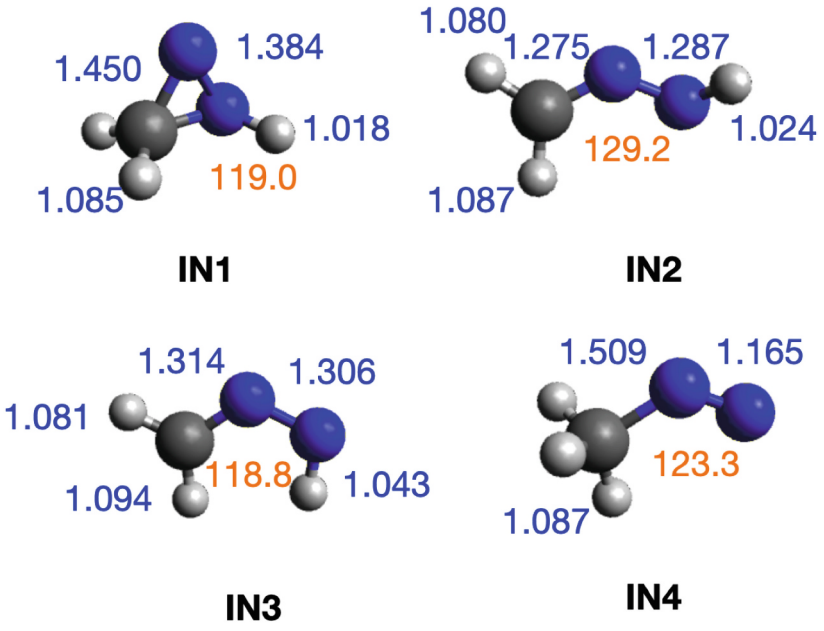

Fig. 3. B3LYP optimized geometries (distances in Å, in blue; angles in orange, in °) of the intermediates identified along the PES for the reaction N(^{2}D)+CH_2NH. (Color figure online)

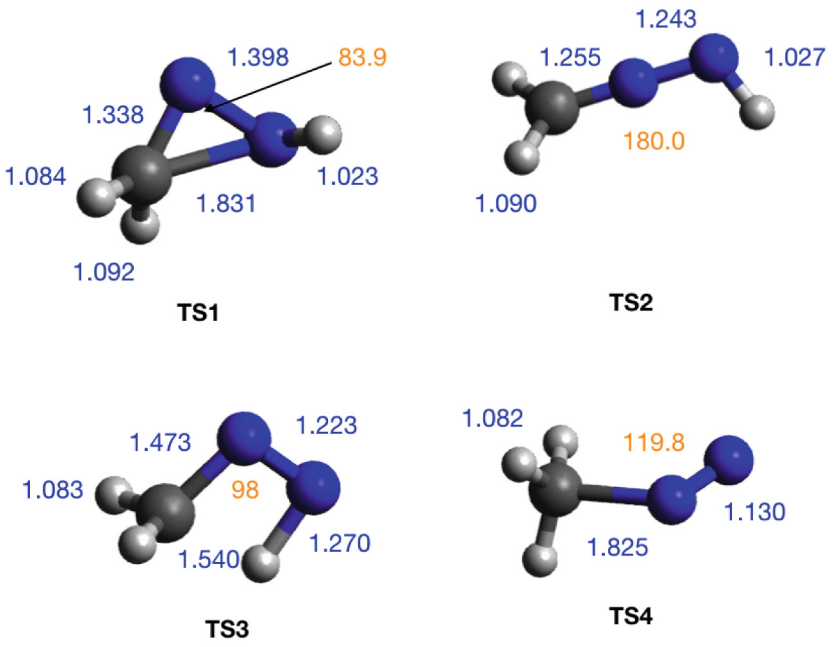

Fig. 4. B3LYP optimized geometries (distances in Å, in blue; angles in orange, in °) of the transition states identified along the PES for the reaction $N(^2D)+CH_2NH$. (Color figure online)

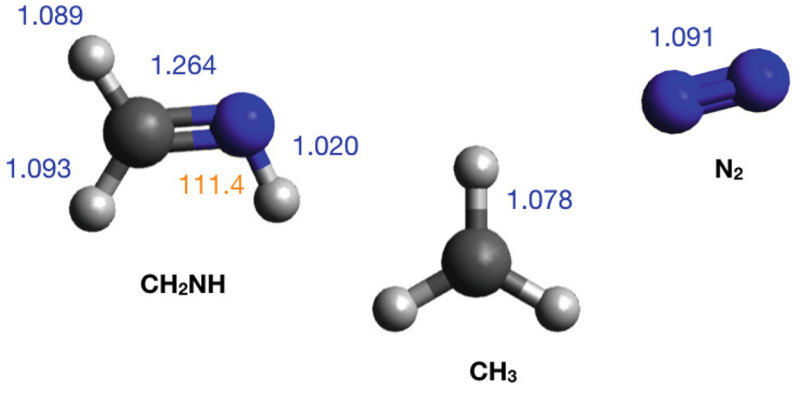

Fig. 5. B3LYP optimized geometries (distances in Å, in blue; angles in orange, in °) of the reactant and products identified along the PES for the reaction $N(^2D)+CH_2NH$ (Color figure online)

4 Discussion

The present results can be compared with a series of previous investigation performed on the reaction of N(^{2}D) with different nitrile species, including acetonitrile (CH_3CN), vinyl cyanide (CH_2CHCN) and cyanoacetylene (HC_3N) [25–27], where the same computational approach was used for the analysis of the PES. In the case of CH_3CN, CH_2CHCN and HC_3N the presence of a submerged barrier along the nitrogen-attack pathway (ranging from −5 to −10 kJ/mol) effectively reduces its competitiveness with respect to alternative addition channels. This behavior can be rationalized by considering the electronic structure of the –CN moiety in the three molecules, where the strong π-bonding orbitals favor attack on the carbon side, while the lone pair on the nitrile nitrogen is stabilized and less available for interaction with the electrophilic N(^{2}D). A different case is represented by the CH_2NH molecule, where the C = N bond is less stabilized than the triple bond in nitriles. Consequently, the reaction proceeds in a barrierless approach toward the formation of a three-membered C–(N)–N cyclic intermediate. This intermediate reflects efficient overlap between the singly occupied orbital of N(^{2}D) and the lone-pair/π system of the imine, without the need to overcome an entrance barrier. The minimum-energy path of the reaction N(^{2}D) + $CH_2NH \rightarrow N_2$ + CH_3 is characterized by local maxima and minima that lie at energies well below the asymptotic energy of the reactants. There is therefore no doubt that this reaction channel is open under the conditions of Titan's thermosphere, where methanimine reaches its maximum mixing ratio, and the N(^{2}D) production rate is at its maximum.

The impact of temperature on the N(^{2}D) + CH_2NH reaction under Titan's thermospheric conditions is expected to be moderate, although not negligible. Since the N(^{2}D) electronic state is highly reactive and the reaction with methanimine is expected to proceed without a significant entrance barrier, the overall rate coefficient should show only a weak temperature dependence, as is typical for barrierless radical-neutral reactions.

Temperature may still affect the reaction by influencing the branching ratios among competing product channels, by modifying the stabilization and lifetime of intermediate complexes, particularly at lower temperatures. Nevertheless, as previously pointed out, these effects are expected to remain limited over the relatively narrow temperature range of Titan's temperature.

In this contribution, we have not explored competing reaction channels that, however, could be present if we consider the N(^{2}D) addition to the C-atom of methanimine. Therefore, to draw definitive conclusions about the importance of this reaction pathway, we need to complete the study and determine the branching ratios for the competing pathways. In all cases, the characterized pathway remains facile and perfectly available under the conditions of Titan's thermosphere.

5 Conclusions

In the present contribution, a theoretical investigation of a possible path in the reaction of N(^{2}D) with methanimine (CH_2NH) was performed combining DFT theory and CCSD(T) approach to characterize the full potential energy surface. The calculations show how the initial attack of N(^{2}D) on the C = N bond of methanimine is barrierless,

in contrast with similar reactions with nitriles such as acetonitrile, vinyl cyanide, and cyanoacetylene, where submerged barriers along the nitrogen-attack pathway reduce the competitiveness of this channel. Subsequent steps leading to the formation of CH_3 + N_2 involve intermediates and transition states that lie significantly below the energy of the separated reactants, confirming that the overall process is exothermic and barrierless with respect to the entrance channel. These findings indicate that the $N(^2D)$ + $CH_2NH \rightarrow CH_3 + N_2$ reaction can be a feasible and efficient pathway under the conditions of Titan's thermosphere, where both reactants are present and abundant. While other potential reaction pathways, characterized by different rearrangements of the initial intermediate, may compete, the present findings show a plausible route for the formation of N_2 in Titan's atmosphere. This work provides a foundation for future theoretical studies, aimed at a detailed analysis of the complete PES, with a focus on quantifying product branching ratios to fully assess the astrochemical impact of this process.

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