Crossed beams and theoretical study on two reactions relevant to Titan's atmosphere: N(²D) + propyne and N(²D) + allene

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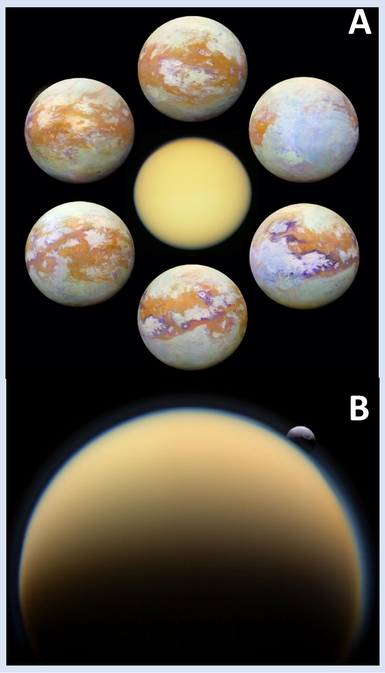
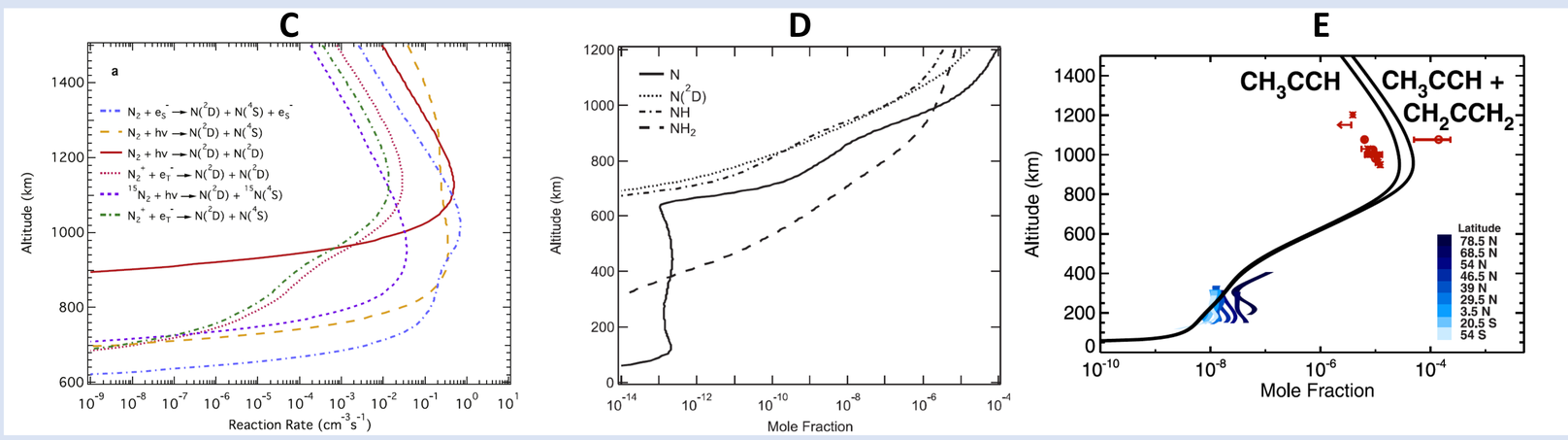
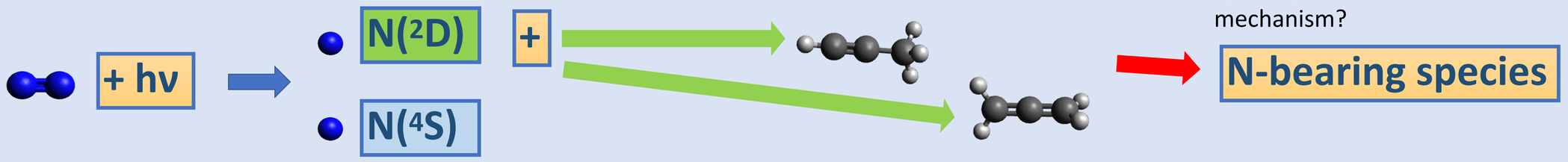
Background





1. Several hydrocarbons have been detected **in the atmosphere of Titan** [1-3]
2. N_2 is dissociated into reactive N atoms [1,4].
3. What are the primary products of **N(²D) + hydrocarbons** (**growth of molecular complexity** *vs.* **fragmentation in smaller species**)? What is the reaction mechanism?



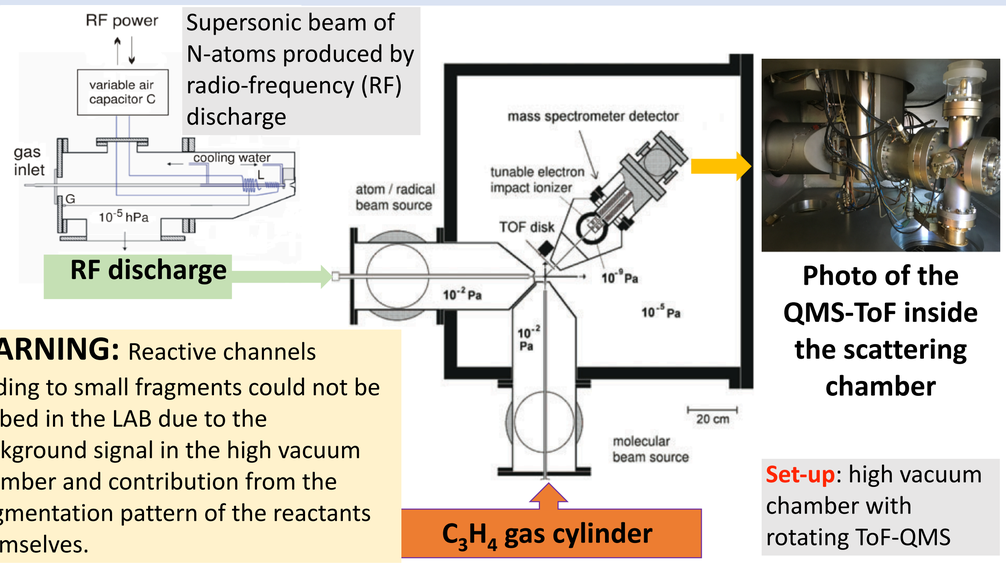
***Figures**: **A**) Titan; taken from https://apod.nasa.gov/apod/ap200820.html **B**) Titan; taken from https://apod.nasa.gov/apod/ap100127.html. **C, D, E**) Figures 30, 31, 45 from ref 1.*

Methods & Aim:

We have investigated the **N(²D) + CH_3CCH** (propyne) reaction and the **N(²D) + H_2CCCH_2** (allene) reaction to elucidate **the nature of the primary products** and the **micromechanism** at play

[Experimental] by coupling the **crossed molecular beams** (CMB) technique with mass spectrometric detection and time-of-flight analysis (**angular distribution** and **tof spectra**)

[Theoretical] with **electronic structure calculations** of stationary points and product energetics (potential energy surface, **PES**). Furthermore, **RRKM statistical calculations** were performed to derive the **product branching ratios (BRs)** under the conditions of the present experiments and of the atmosphere of Titan.



WARNING: Reactive channels leading to small fragments could not be probed in the LAB due to the background signal in the high vacuum chamber and contribution from the fragmentation pattern of the reactants themselves.

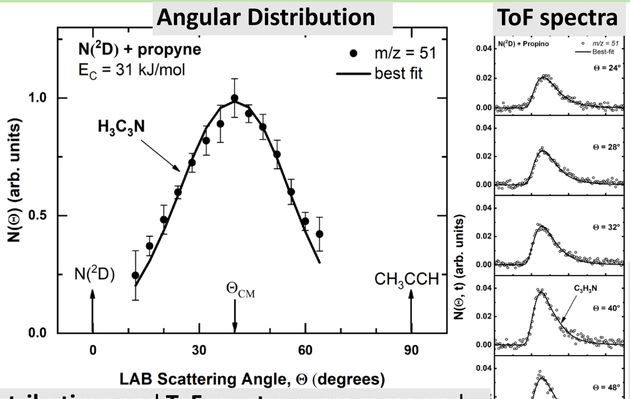
Photo of the QMS-ToF inside the scattering chamber

Set-up: high vacuum chamber with rotating ToF-QMS

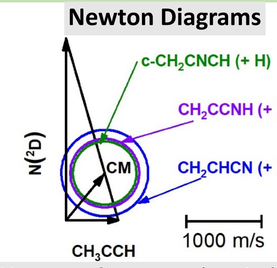
Results

LAB data and analysis

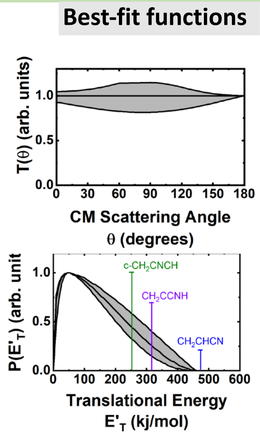
N(²D) + CH_3CCH



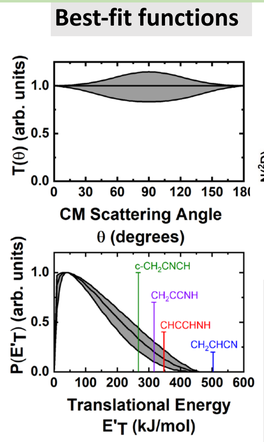
Angular distributions and **ToF spectra**: were measured for the product (daughter ion) at m/z=51 (best S/N).

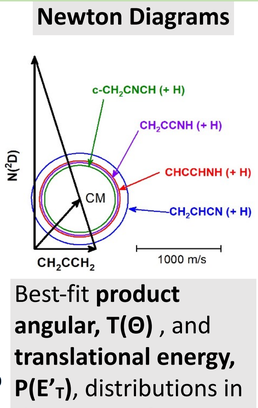


Newton diagram: the circles delimit the maximum velocity of the indicated products if all the available energy is channeled into product translational energy.

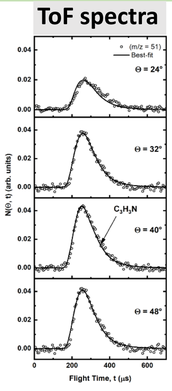


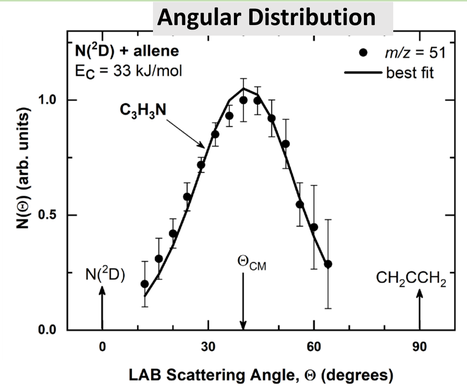
N(²D) + H_2CCCH_2



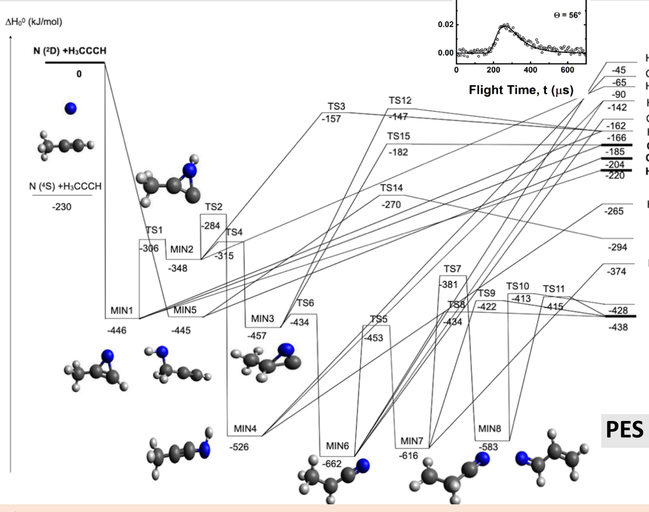


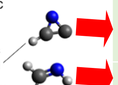
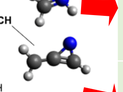
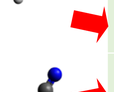
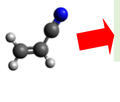
Best-fit **product angular, T(Θ)** , and **translational energy, P(E'T)**, distributions in the centre-of-mass frame were obtained from a forward convolution analysis of the LAB angular and TOF distributions.





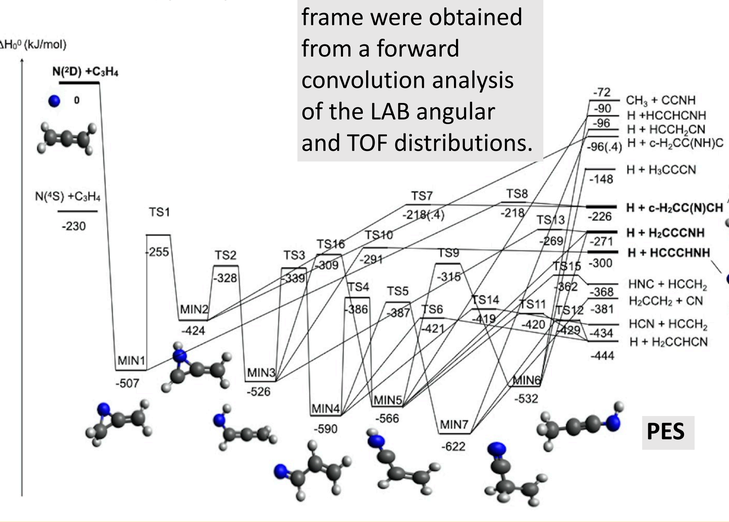
PES and RRKM

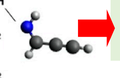


	94 K	175 K	300 K	EXP
	28%	28%	29%	32%
	41%	41%	41%	41%
	4%	4%	4%	4%
	16%	16%	15%	12%

BRs

PES → Theoretical **BRs** from **RRKM** statistical calculations.



	94 K	175 K	300 K	EXP
	86%	86%	86%	87%
	1%	1%	1%	1%
	11%	11%	11%	10%

BRs

PES: B3LYP/aug-cc-pVTZ: geometry opt. and harmonic frequencies.
CCSD(T)/aug-cc-pVTZ: single point for energies

Key results

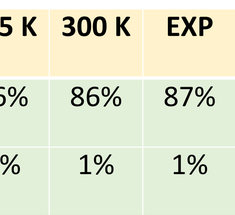
- The **H-elimination/N-addition channel** was observed for both the reactions at the laboratory conditions.
- Experimental data alone cannot not resolve the contribution from the different isomers to the measured signal (m/z).
- The H-elimination/N-addition channels occur *via* an **indirect mechanism** through the formation of a **long-lived complex**.
- Electronic structure calculations: **barrierless reactions** with **a nearly identical PES**...
- ... but the two systems evolve towards **completely different outcomes** as it highlighted by the theoretical **BRs**.
- The main channels for **N+CH_3CCH** are those that **break the molecule into smaller species** (CCH+H_2CNH and CH_3+c-C(N)CH), whereas **N-addition dominates** for the **N+H_2CCCH_2** reaction.
- Focussing only on the H-elimination/N-addition channel for both the systems, we found two qualitatively reversed situations: the linear isomer is favoured over the cyclic one for **N+CH_3CCH**, while the cyclic isomer is favoured over the linear one for **N+H_2CCCH_2** .

Astrophysical implications

CH_3CCH and H_2CCCH_2 constitute the first hydrocarbon isomer pair detected on Titan. Their abundances is comparable to that of N(²D) in the upper atmosphere of Titan, and hence the two reactions of our study can take place efficiently at those altitudes (around 1000 km). By leading to different types of products, these two systems cannot be treated as the same in the astrochemical models and **their divergent reactivity should be taken into account**. It is noteworthy to highlight that **N+CH_3CCH** is a **viable route to the synthesis of vinyl cyanide (H_2CCHCN)**.

H_2CCHCN was recently mapped in Titan's atmosphere and proposed as an ideal candidate to form cell membranes/vesicle structures in Titan's hydrocarbon-rich lakes and seas [5-7](Figures F and G).

***Figures**: **F**) Figure 3 from ref 7.*
***G**) Titan's lakes; taken from* https://apod.nasa.gov/apod/ap070207.html



References

[1] V. Vuitton et al., *Icarus*, **324**,120 (2019)
[2] N. A Lombardo et al., *Icarus*, **317**, 454 (2019)
[3] N. A Lombardo et al., *Astrophys. J.*, **881**, L33 (2019)
[4] P. Lavvas et al., *Icarus*, **213**, 233 (2011)
[5] J. C.-Y. Lai et al., *Astron. J.*,**154**, 206 (2017)
[6] M. Y. Palmer et al., *Sci. Adv.*, **3**: e1700022 (2017)
[7] Stevenson et al. *Sci. Adv.* **1**:e1400067 (2015)

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