Hydrogenation of solid hydrogen cyanide HCN and methanimine CH_2NH at low temperature

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By
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Background…

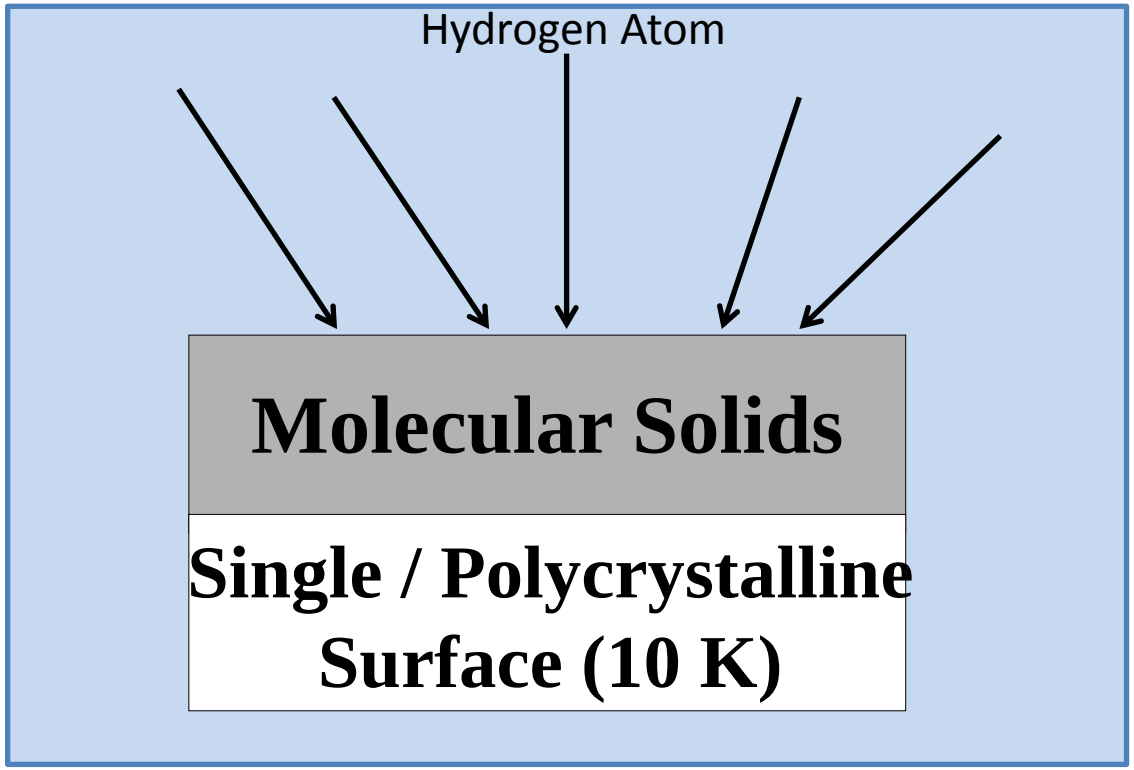
- Chemistry deals with molecular transformations……past to future
- Interstellar chemistry:- reactions in space. (low temperature <10K; extreme high vacuum ~10^{-15} mbar).
- No thermal activation, no collisional activation.
- A kind of non-thermal non-equilibrium reaction kinetics takes place.
- ISM has mainly 2 parts: Gas and Dust
- It's the same molecules, but it's a different kind of chemistry takes place.

"If you are a gas atom, you might collide with another one every day or so, instead of the billions of collisions per second that take place in a gas at atmospheric pressure".
By **Eric Herbst (Ohio State University).**

- http://www.chem.hawaii.edu/Bil301/solidstate.html
- http://www.rsc.org/chemistryworld/News/2005/October/19100501.asp
- http://www.physics.ohio-state.edu/~eric/research_files/cen.htm

Introduction

- Surface hydrogenation play an important role in the evolution of molecules on interstellar ices.
- Especially at low temperature in dense molecular clouds where the secondary photon field is very weak and where hydrogen atoms have an important residence time on the surface.



- Various studies show that hydrogenation of CO gives H_2CO and CH_3OH.*
- O_2 and O_3 hydrogenation gives Solid H_2O.**
- Hydrogenation of a CO:O_2 mixture gives HCOOH.***
- Hydrogenation of CH_3CHO gives C_2H_5OH, CH_3OH, H_2CO and CH_4.****

In this paper……

- They bombarded solid hydrogen cyanide (HCN) and methanimine (CH_2NH) with warm H-atoms.
- Ice analog composition were monitored by FT-RAIRS, and the hydrogenation products were analyzed by TPD experiments.
- The product obtained was methylamine (CH_3NH_2).

*Hiraoka et al. 1998, ApJ, 498, 710; **Dulieu et al. 2010, A&A, 571, ***A30; Ioppolo et al. 2011, MNRAS,410, 1089; ****Bisschop et al. 2007, A&A, 474, 1061

Why HCN ??????

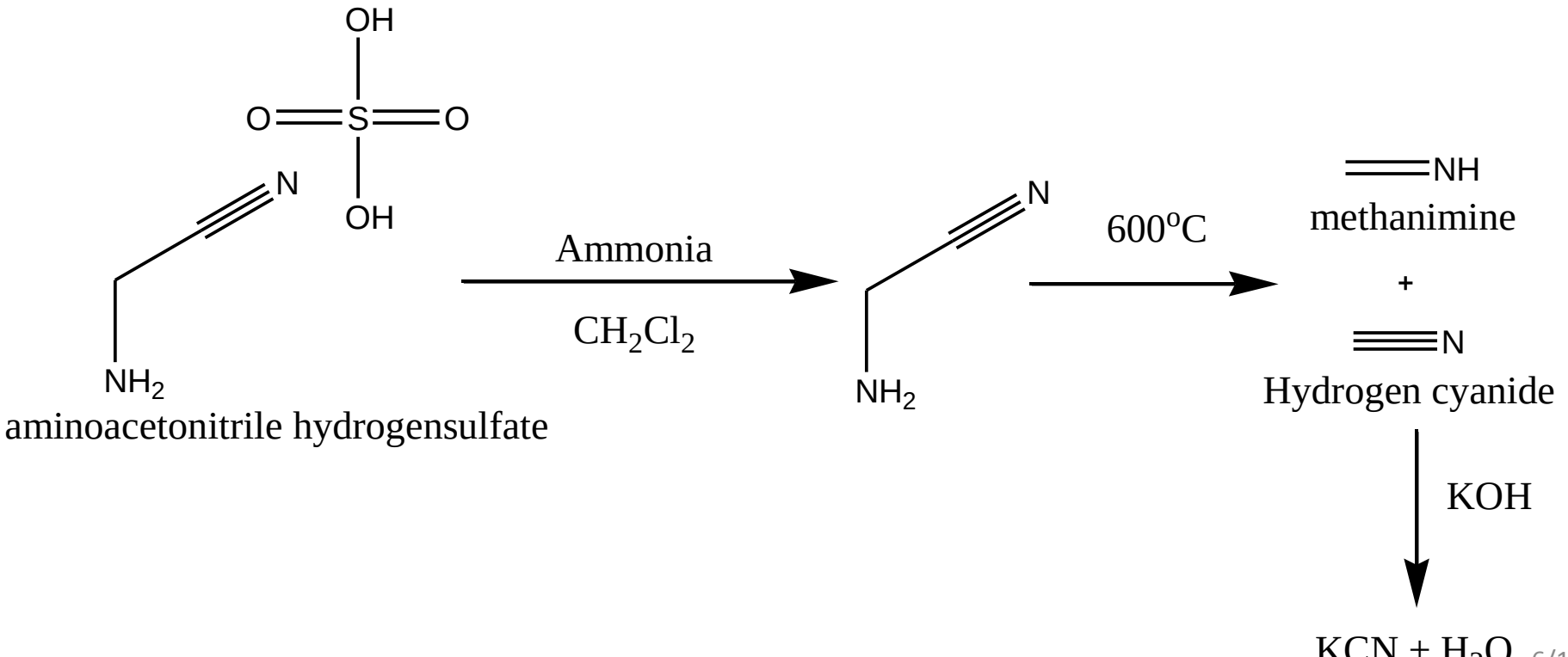
- HCN is important in interstellar chemistry because it is the simplest molecule containing CN moiety which is a prerequisite to form amino acid.*
- It has been shown that CH_3NH_2 can thermally react with CO_2 in the solid phase to form a carbamate, which can be converted into a glycine salt under VUV irradiation.**
- This glycine salt eventually desorbs as gas-phase-neutral glycine (NH_2CH_2COOH).

*Ferris et al. 1984, Tetrahedron, 40, 1093; **Bossa et al. 2009, A&A, 506, 601

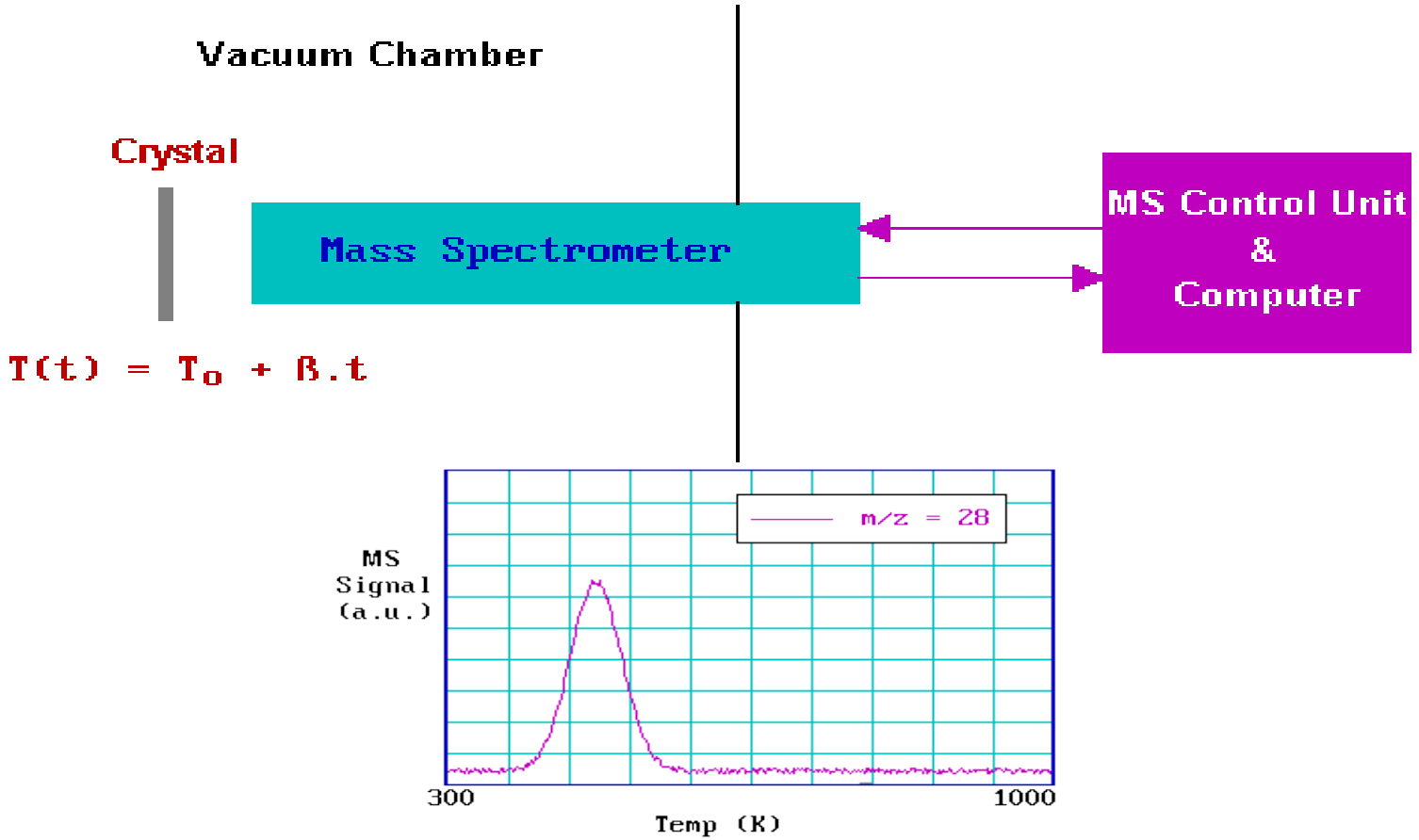
Experimental Section

- A UHV chamber with a polished copper surface maintained at 15 K by a closed cycle He cryostat and heated by a temperature controller; temperature measured by a silicon diode sensor which is having 0.1 K uncertainty
- Gas phase species are measured by RGA-QMS and all TPD done with 5 K min^{-1} ramping rate. Surface species measured by FT-RAIRS.
- Warm atomic Hydrogen was produced from a molecular hydrogen source (2.4 GHz microwave discharge).
- Atomic hydrogen flux was calibrated by hydrogenating CO ice at 15 K and measuring the H_2CO band at 1720cm^{-1} and is calculated to be 1014 cm^{-2} s^{-1}.

- HCN was synthesized from thermal reaction of KCN and excess stearic acid $CH_3(CH_2)_{16}COOH$ in a primary pumped vacuum line.
- CH_2NH was obtained from the dehydrocyanation of NH_2CH_2CN which was done in by bubbling ammonia through $NCCH_2NH_3^+HSO_4^-$ suspended in CH_2Cl_2.

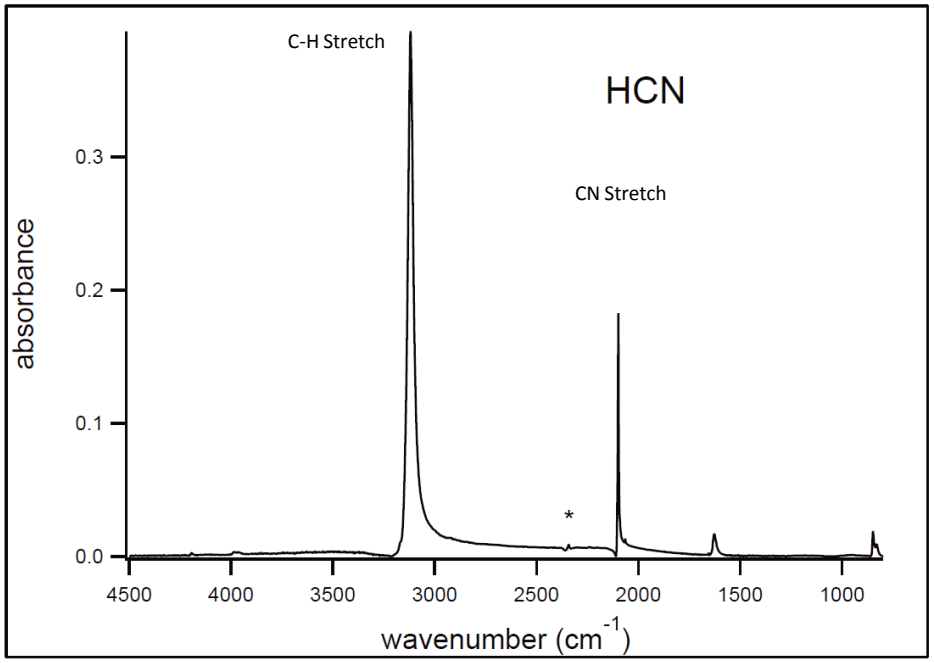


Temperature Programmed Desorption (TPD) spectroscopy

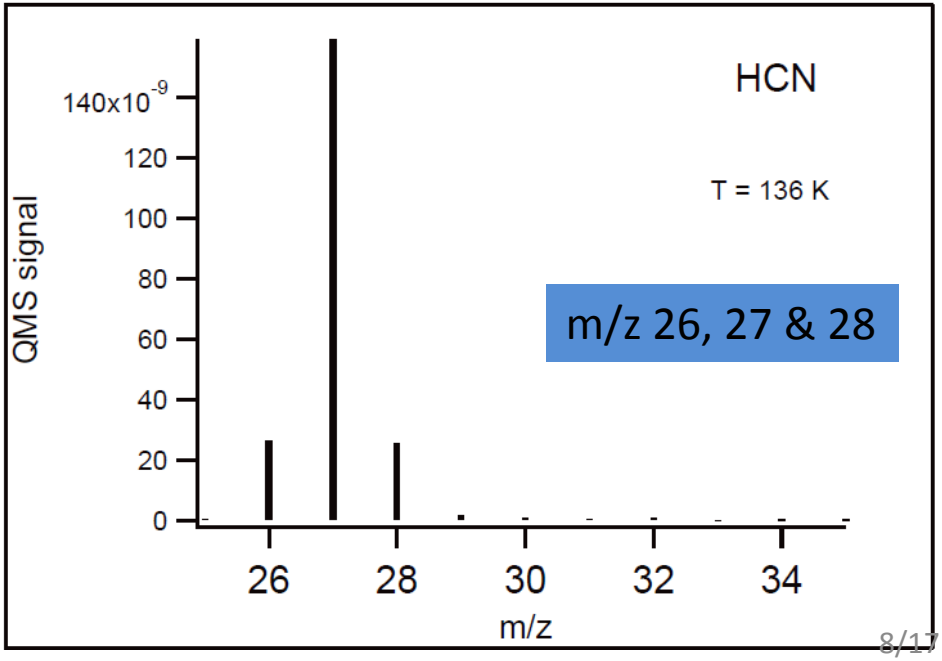


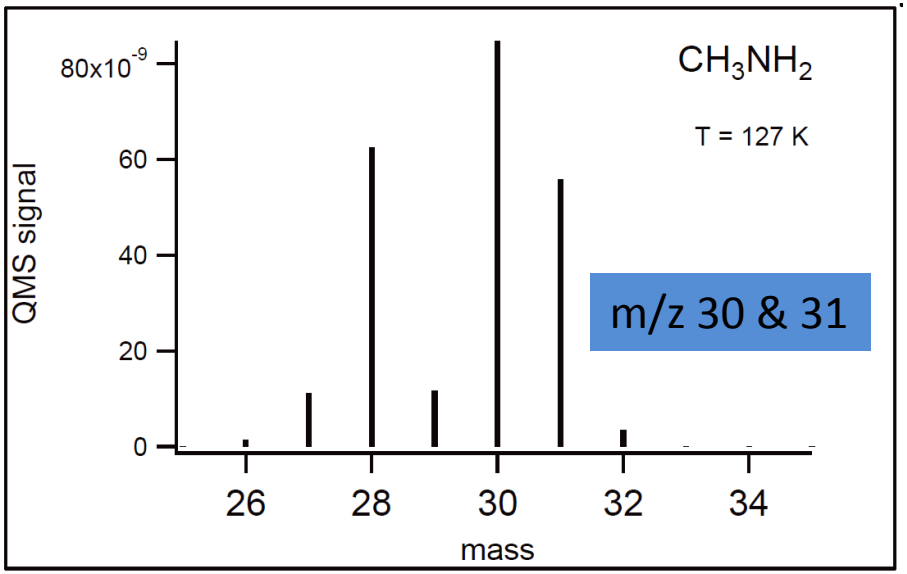
Results and Discussion

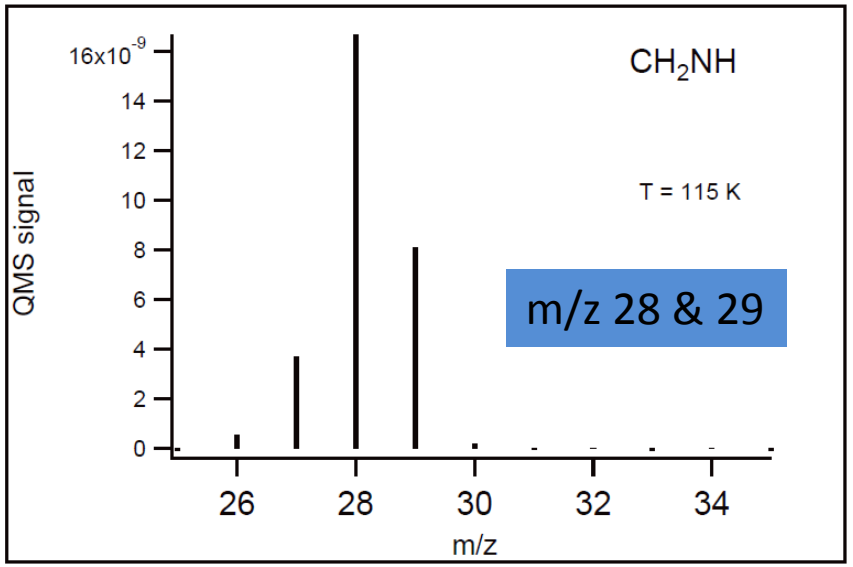
1. Hydrogenation of pure hydrogen cyanide HCN



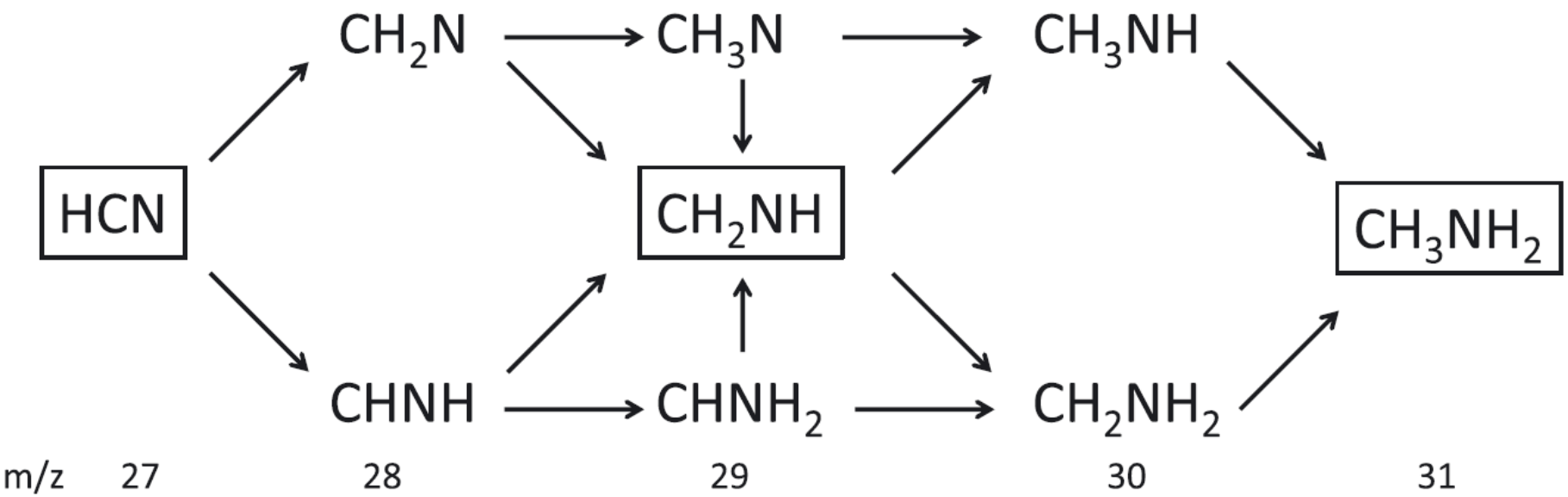
Pure HCN infrared spectrum at 15 K before hydrogenation. Peak at 2349 cm^{-1} corresponds CO_2 issued from the decomposition of stearic acid during the HCN synthesis and the mass spectrum of HCN at 114 K



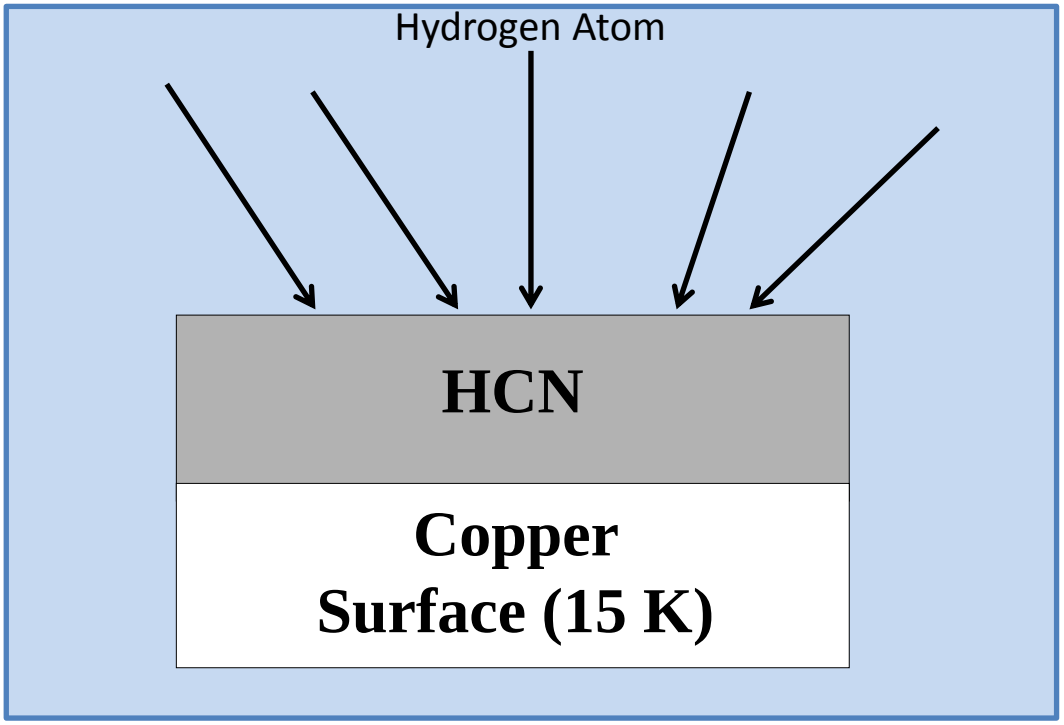




Mass spectra of methanimine CH_2NH and methylamine CH_3NH_2 at T = 115 K and T = 126 K respectively. Below is the proposed reaction scheme for the hydrogenation of HCN with their corresponding m/z values



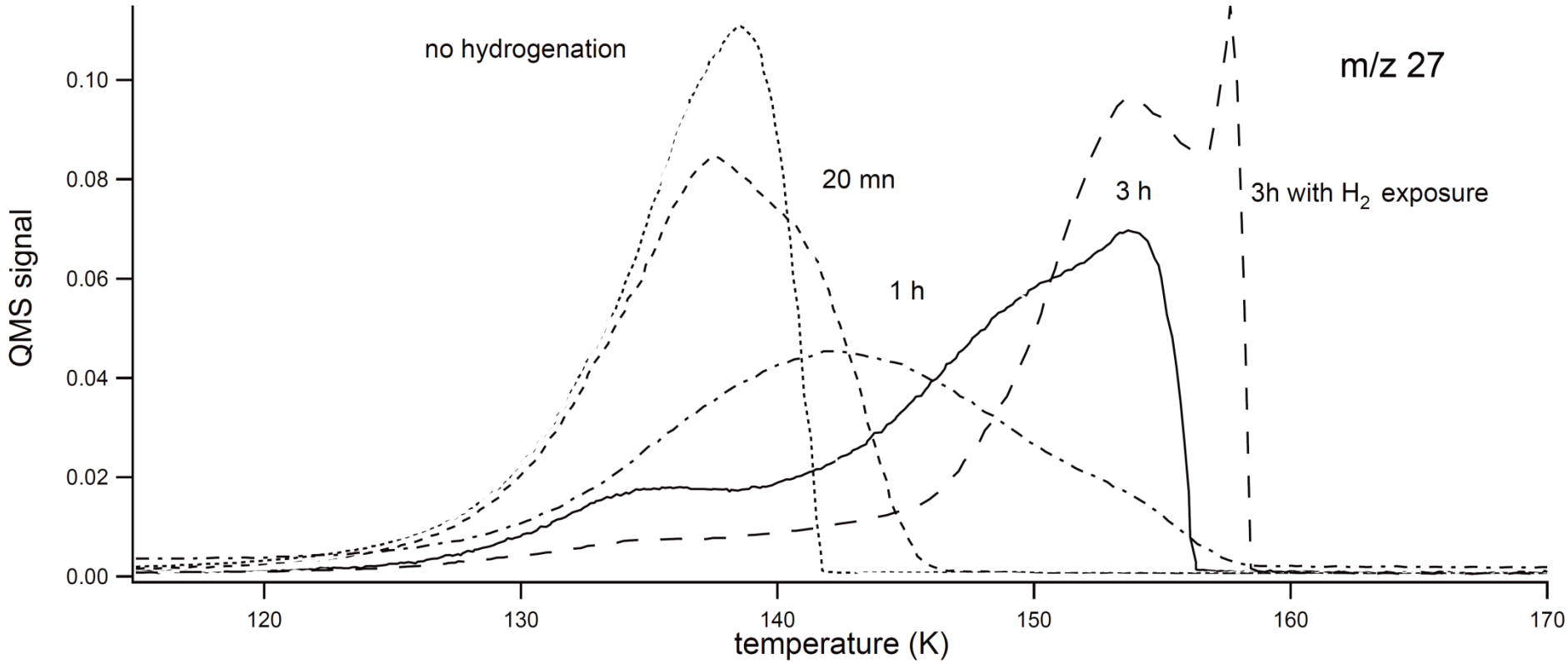
Reaction Scheme 1



Time of exposure

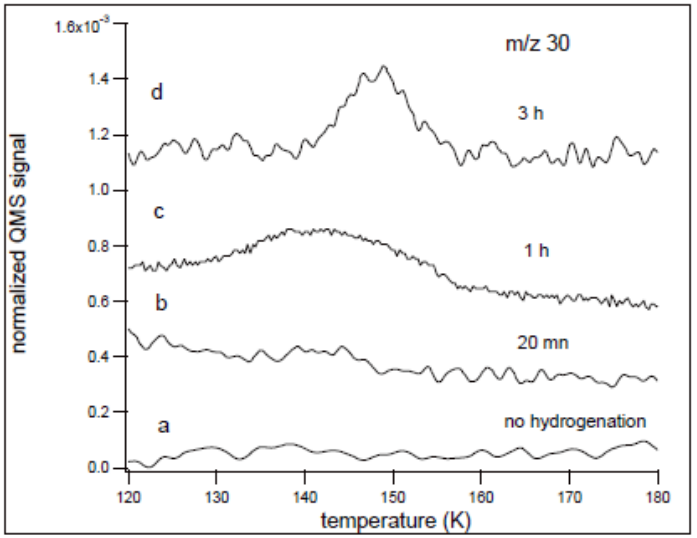
a) 0 min
b) 20 min
c) 1 hr
d) 3 hr
e) 3 hr with H_2

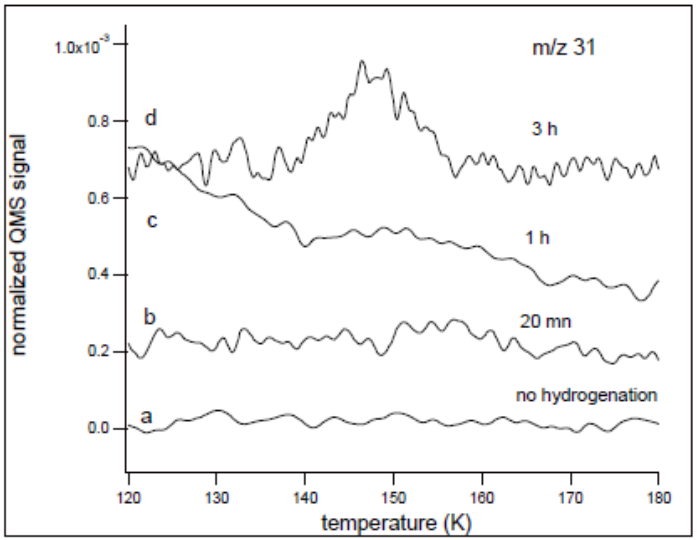
TPD done at 5 K min^{-1} ramping rate. Mass selected were 27, 28, 29, 30 and 31



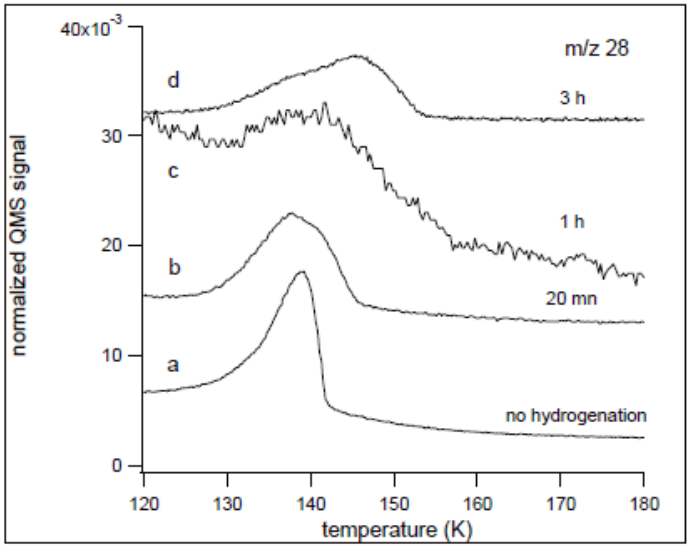
Temperature-programmed desorption curves of *m/z 27 of hydrogen* cyanide HCN without exposure to the room-temperature atomic H-beam at 15 K (dotted line), and with exposure during 20 min (dashed line), one hour (dotted-dashed line) and three hours (full line). The warm atomic H_2 beam induces a change in morphology that shifts the desorption maximum to higher temperatures, as shown by the TPD curve obtained after three hours exposure to the H_2 beam with the plasma discharge off (large dashed line).

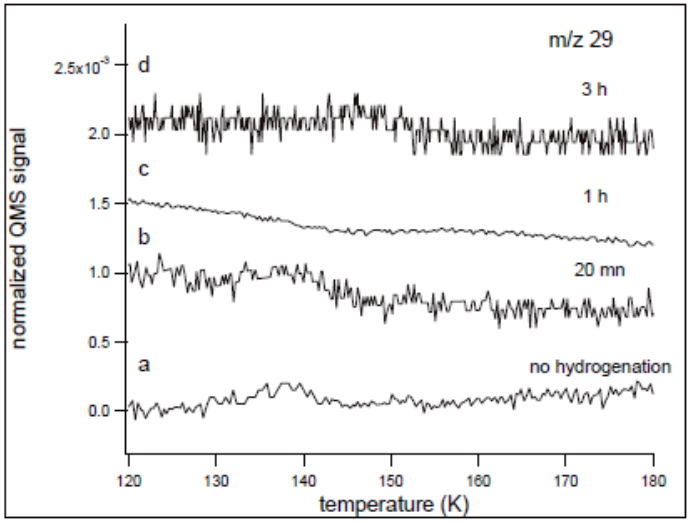
CH_3NH_2 Species





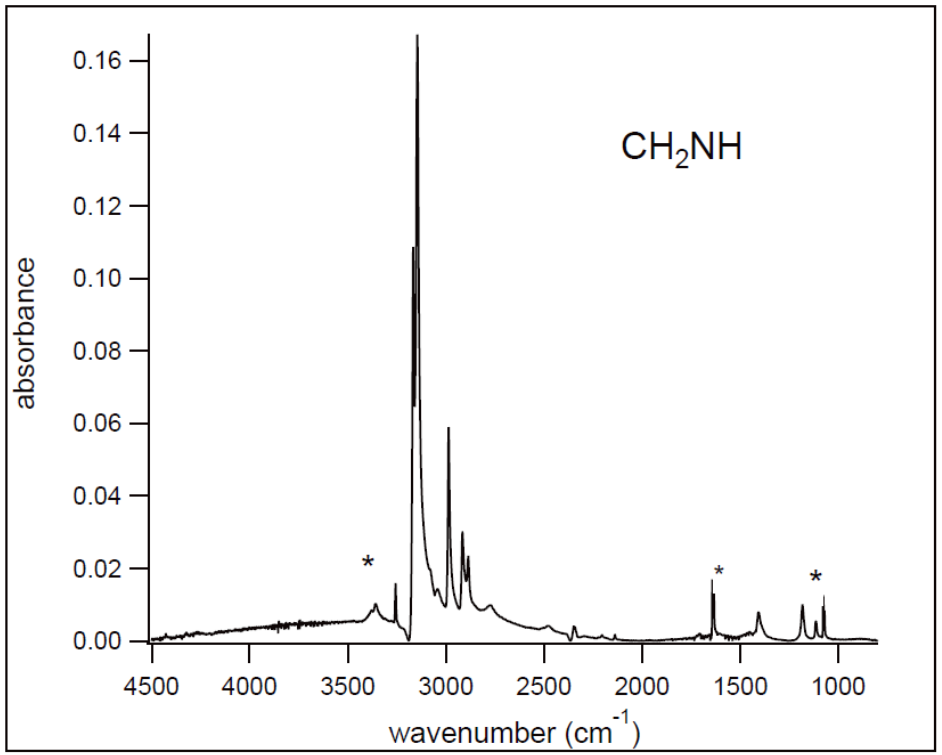
CH_2NH Species



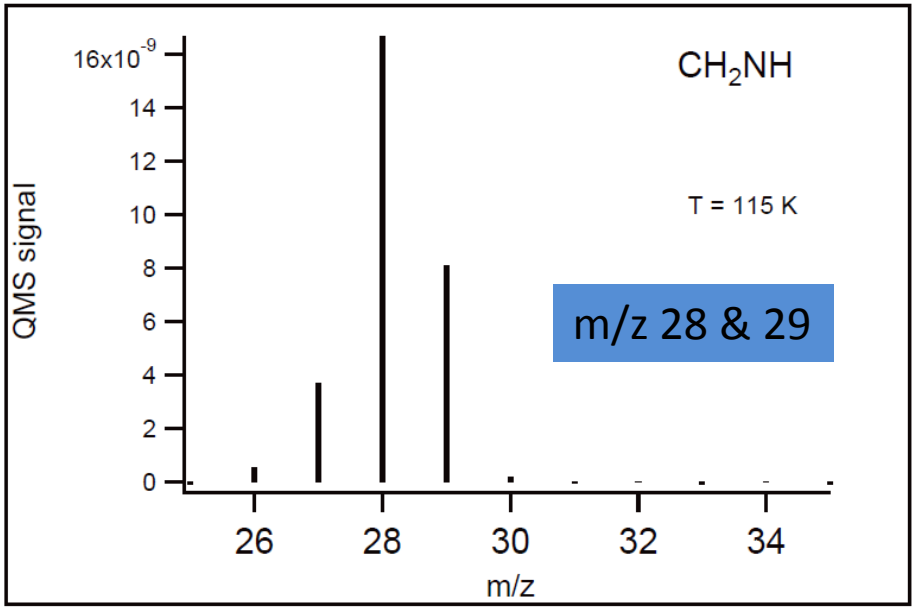


Temperature-programmed desorption curve at *m/z 30 ,31, 28 and 29 of* HCN without exposure to the atomic H beam (a) and after 20 min (b), 1 h (c) and 3 h (d) exposure at 15 K; *m/z 30 and 31 evidence the formation* of methylamine CH_3NH_2 from the hydrogenation of HCN; *m/z 28* shows the change in morphology of HCN during the hydrogenation experiment. No contribution from CH_2NH is visible in the *m/z 29 curve.*

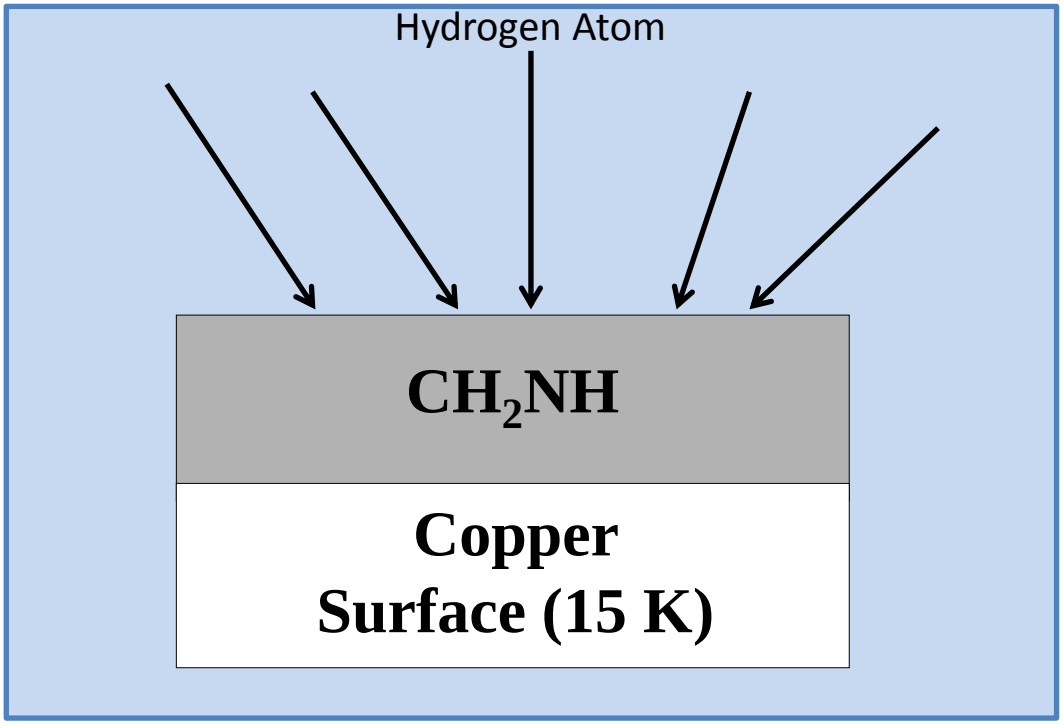
2. Hydrogenation of methanimine CH_2NH



Pure CH_2NH infrared spectrum at 15 K before hydrogenation. The bands at 1010, 1628 and 3377 cm^{-1} correspond to NH_3 remaining from CH_3NH synthesis, the proposed reaction scheme and the mass spectra of CH_3NH at 115 K



Reaction Scheme 2

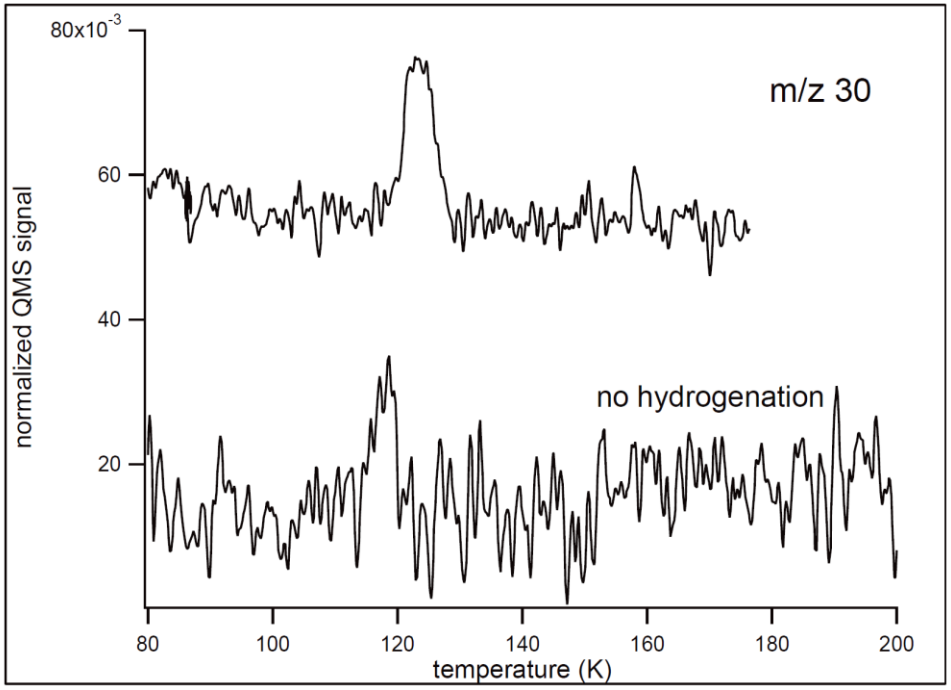


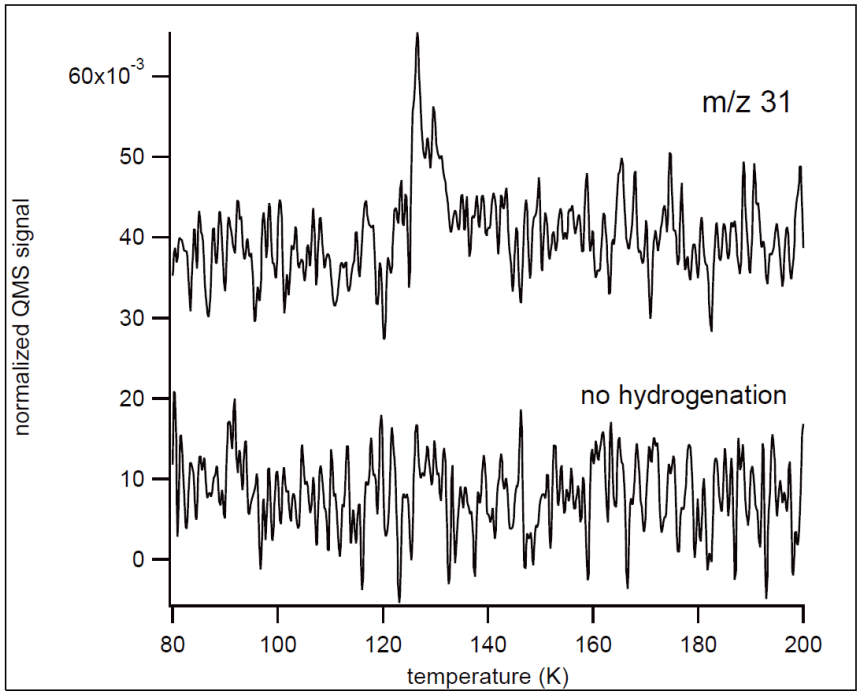
Time of exposure

a) 0 min

b) 2 hr

TPD done at 5 K min^{-1} ramping rate.
Mass selected were 30 and 31





Temperature-programmed desorption spectra of methanimine CH_2NH after hydrogenation for m/z 30 and m/z 31 at T = 15 K. The TPD spectrum of CH_2NH without hydrogenation is shown in the lower part of the figures for the two masses.

Conclusion

- HCN can be hydrogenated to the fully saturated species CH_3NH_2 at low temperature.
- A possible hydrogenation reaction scheme was proposed in which CH_2NH was the stable intermediate.
- But in the experiment they were not able to observe CH_2NH and only CH_3NH_2 was observed.
- A separate hydrogenation reaction of CH_2NH also gave CH_3NH_2.
- This work shows that it is possible to hydrogenate a C≡N bond in interstellar conditions

Future plans??

- Collision with D/D^+ gives more insight into the reaction mechanism.
- HCN on various other surfaces (like H_2O, EtOH ice) can trigger/ catalyze other reactions which can be studied.
- Presence of UV radiation may change the reactivity significantly.

Thank you all….