The ROSINA Perspective on the CN/HCN Ratio at Comet 67P/Churyumov-Gerasimenko

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Welcome!☺

Content

(1) The CN Riddle

From remote observations:

- [1-2]: HCN production rate upper limit smaller than the CN production rate for comet IRAS-Araki-Alcock
- [3]: CN parent Haser scale length cannot be associated with HCN photodissociation alone
- [4]: Possible explanations:
  - Degrading volatiles other than HCN
  - Degrading refractories

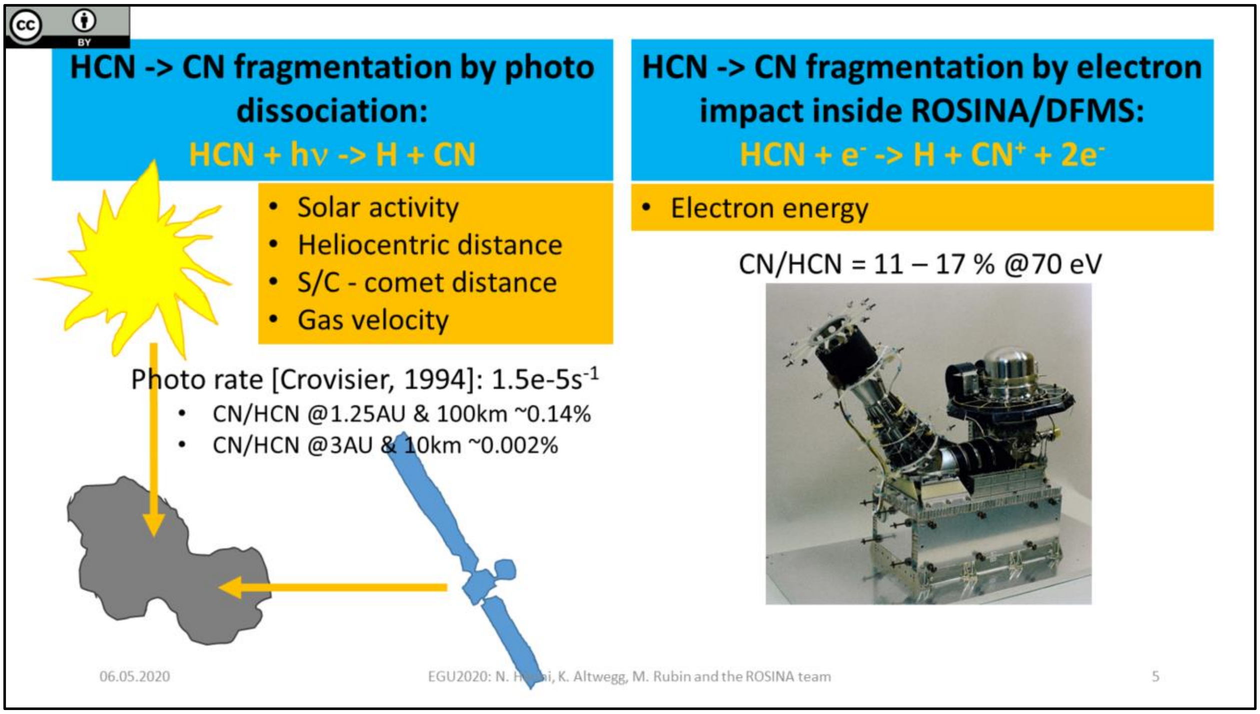
[1] Bockelée-Morvan et al. Astron. Astrophys. 141 (1984) 411-418.
[2] A'Hearn et al. (1983).
[3] Bockelée-Morvan et al. Astron. Astrophys. 151 (1985) 90-100.
[4] Fray et al. Planetary and Space Science 53 (2005) 1243-1262.

(2) Observing 67P with ROSINA/DFMS

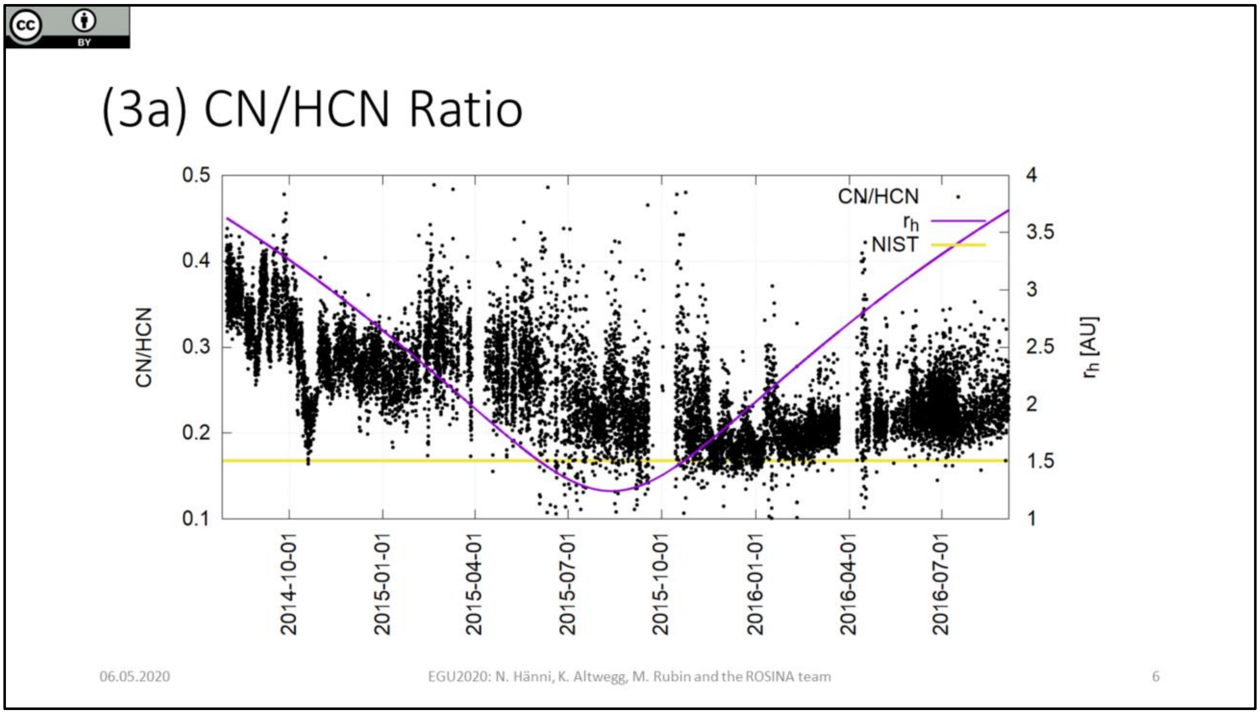
Double focusing mass spectrometer (DFMS) [1]:

- Part of the ROSINA sensor package on Rosetta
- Sector field EI-MS (Mattauch-Herzog configuration)
- Ionization voltage: 45 eV
- Mass range: 12-180 m/z
- Resolution: m/Δm = 3000 (at 1% peak height, m/z = 28)

[1] Balsiger et al. Space Science Reviews 128 (2007) 745-801.



Photodissociation is a **variable** process (due to several variable factors indicated on the slide), while fragmentation under electron impact inside DFMS is a **constant** process (depends only on the energy of the ionizing electron).



HCN and other CN-bearing molecules produce CN inside DFMS with a constant ratio! This ratio was not measured directly on DFMS due to the toxicity of the molecules, but e.g. for HCN (which is by far the most abundant CN-bearing volatile observed at 67P, see next slide) various values are reported in literature:
-0.17 [NIST]
-0.148 [Kusch et al. Phys. Rev. 52 (1937) 843-854]
-0.11 [Stevenson. J. Chem. Phys. 18 (1950) 1347-1351]

-> We observe variable ratios between ~0.15 and ~0.40, as shown in the figure. The NIST value for CN/HCN is indicated by a yellow line for reference. As DFMS operates with a 45 eV electron beam, while NIST uses 70 eV, the CN/HCN ratio observed with DFMS should be a bit lower than the one reported in NIST.

CN-bearing volatiles at 67P seen by ROSINA/DFMS:

parent species	chemical structure	bulk abundance rel. to water in % [1]	CN/parent	References of the fragmentation patterns
hydrogen cyanide	HCN	0.14±0.04	0.168	NIST
hydrogen isocyanide	HNC			
acetonitrile	CH_3CN	0.0059±0.0034	0.016	AIST
methyl isocyanide	CH_3NC		0.020	NIST/R. G. Gillis, Aust. Sci. Service
isocyanic acid	HNCO	0.027±0.016	0.019 or 0.024	Fischer et al. Z. Naturf. 2002 or Bogan et al. J. Phys. Chem. 1971
cyanic acid	HOCN			
formamide	NH_2COH	0.0040±0.0023	0.013	AIST
nitrosomethane	CH_3NO		0.029	NIST
formaldehyde oxime	CH_2NOH			
cyanoacetylene	HCCCN	0.00040±0.00023	0.034	NIST
isocyanoacetylene	HCCNC			
cyanogen	NCCN	single detections	0.047	NIST/A.A.Kutin, Moscow, Russia
isocyanogen	CNCN			

[1] M. Rubin et al. MNRAS 489 (2019) 594-607.

Possible volatile candidates discussed in literature and reviewed thoroughly e.g. by Fray et al. (2005):

HNC -> wrong scale length

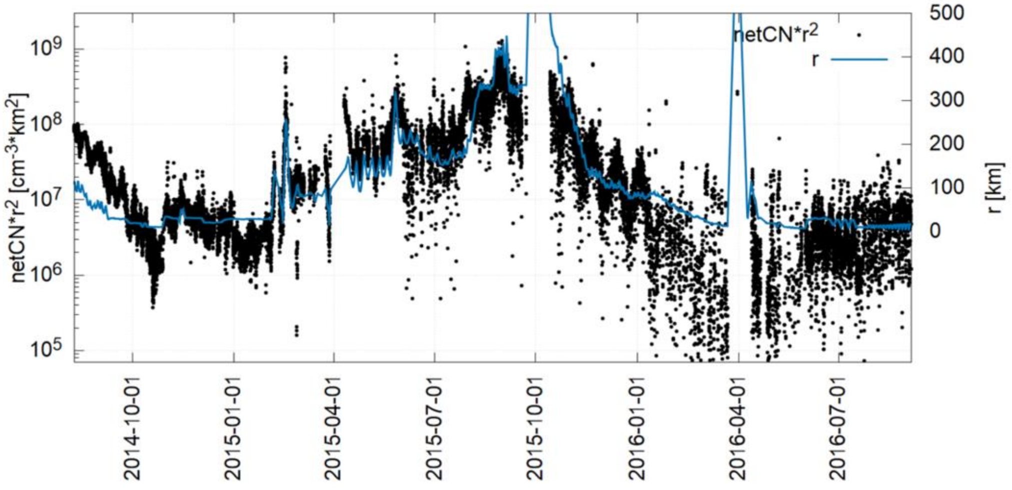
CH_3CN -> quantum yield could be lower than 0.02 [Kanda et al. 1999], wrong scale length

HC_3N -> quantum yield could be lower than 0.05 [Halpern et al. 1988], no sufficiently high production rate

C_2N_2 -> literature values divergent, no allowed rotational transition, vibrational band strength low, high detection limit!

-> If we subtract the CN-signal produced as fragment from HCN as well as other minor CN-bearing species, we still get a lot of residual CN, let's call it netCN!

(3b) netCN



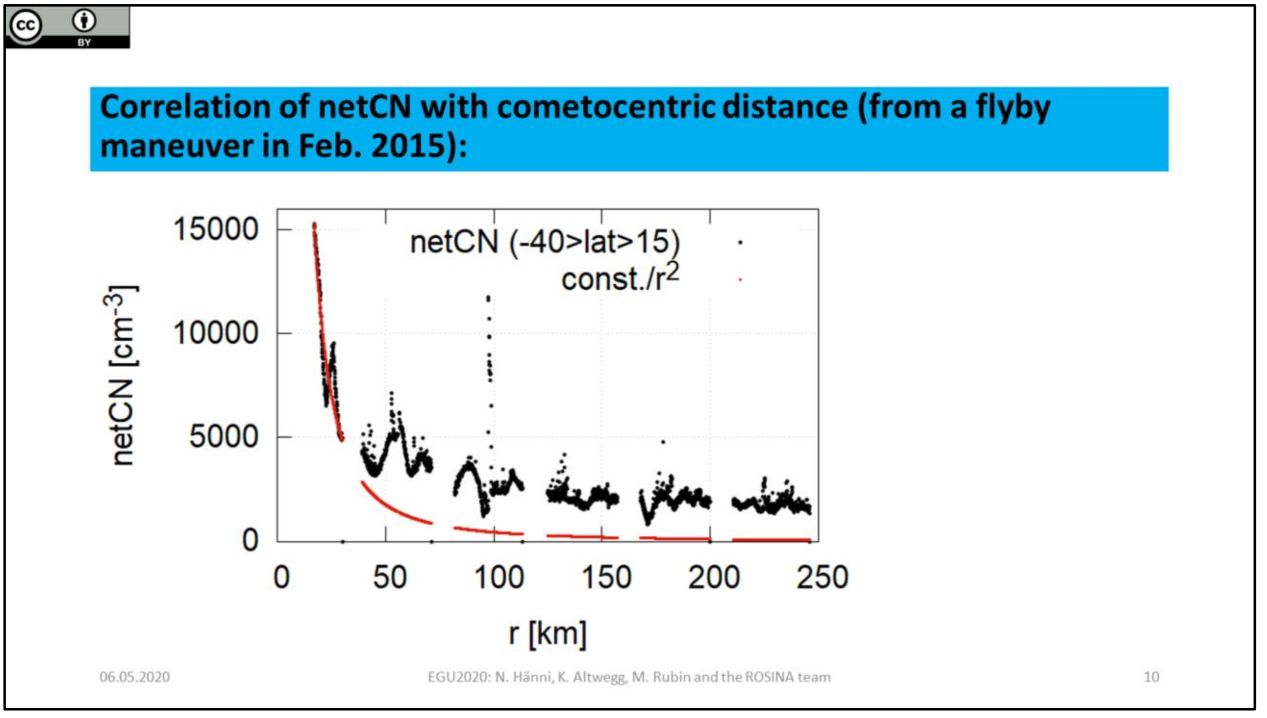
netCN is the portion of the CN-signal observed by ROSINA/DFMS, which cannot be explained by fragmentation of HCN or other CN-bearing volatiles.

-> Interestingly, netCN*r^2 (abundance corrected for free radial outflow) is not flat but seems to be correlated with the cometocentric distance r (shown in blue).

(4) Correlations

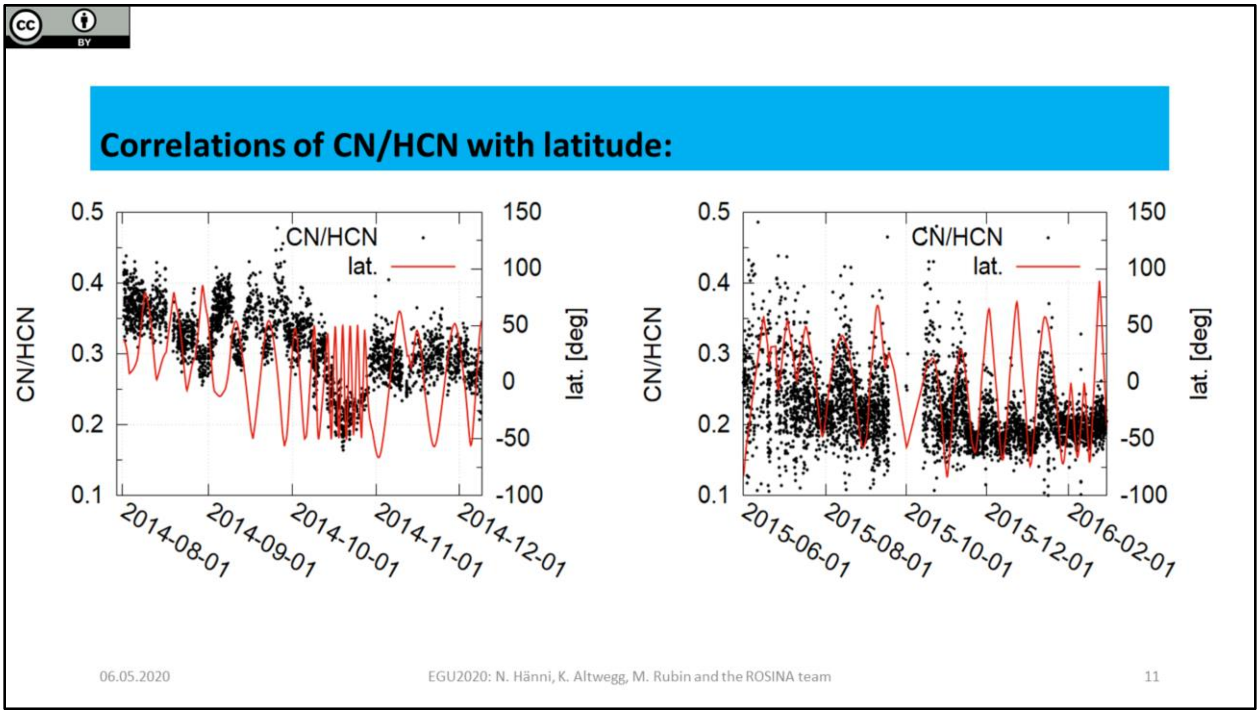
What does this additional CN (netCN) correlate with?

- Cometocentric distance r
  - Indications for a distributed source
- Latitude
  - Beginning of mission: netCN mainly from south
  - Perihelion passage: netCN mainly from north
- Main volatile species
  - Beginning of mission: H_2O mainly from north, CO_2 mainly from south



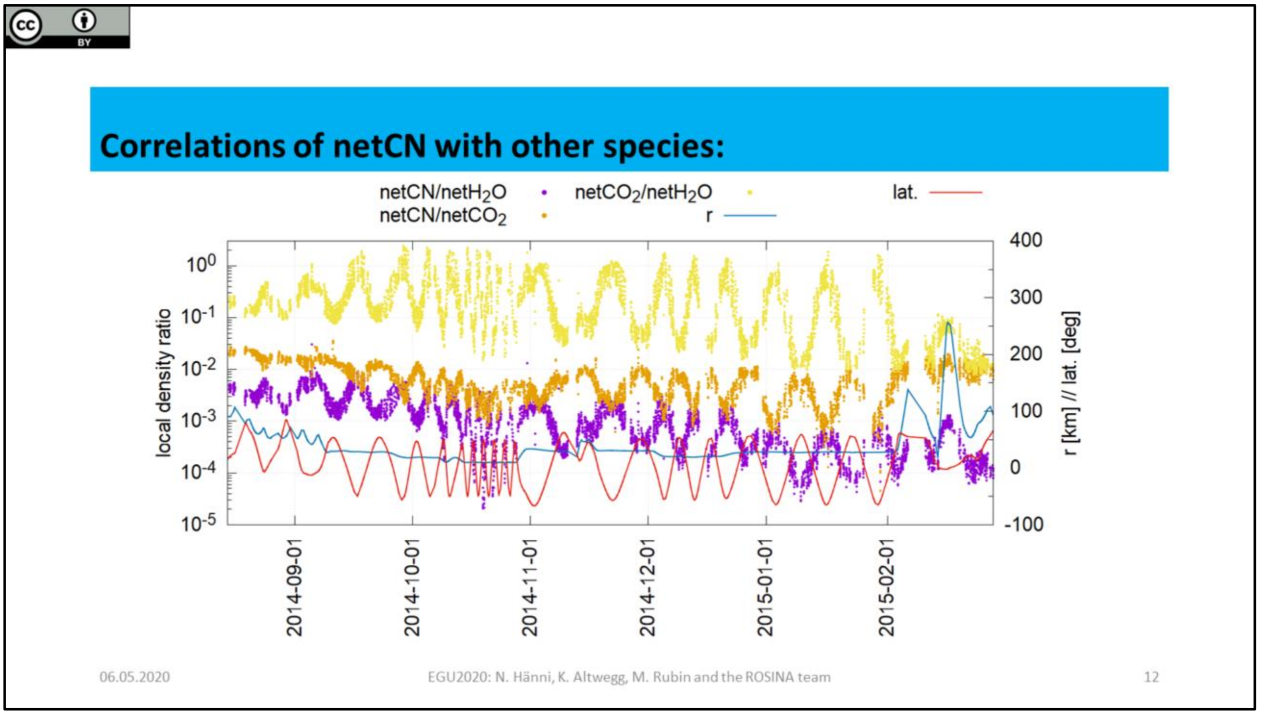
From a flyby event in Feb. 2015, the radial local density of netCN can best be obseved as the other observational parameters change as little as possible. Thered line in the figure is a guide to the eye, showing a decreasing local density according to const./r^2, where const. is a constant able to reproduce the initial values and r is the cometocentric distance. Obviously, the red line underestimates the the density further from the comet.

-> netCN seems to (partially?) originate from a distributed source.



(left) In the beginning of the mission, the CN/HCN ratio is high over the southern latitudes.
(right) Around perihelion, the CN/HCN ratio is high rather over the northern latitudes.
During aphelion, the northern hemisphere experiences a long and little intense summer, while during perihelion, the southern hemisphere experiences a shorter and intense summer.

-> This is inversion probably indicates that seasonal variations play a crucial role regarding the emission of netCN.



The ratios of netCN with the two main species H2O and CO2 show a lot of variations (apparently correlated with latitudinal variations). While netCN/netH2O is high over the southern hemisphere, netCN/netCO2 is high over the northern hemisphere. netCO2/netH2O is plotted for reference. It is high over the south as most of the water is coming from the north, while most of the CO2 is coming from the south, also see Läuter et al. (2019).

(5) Conclusion and Outlook

Hypothesizing about the origin of this additional CN:

a) Degradation of CN-bearing volatiles?
   - No

b) Degradation of CN-bearing refractories?
   - Probably

Based on our analysis we can rule out CN-bearing volatiles as possible parent species to the netCN we observe with DFMS (this netCN may be the long-known CN-radical). A less volatile source seems more likely. It could also be responsible for the observed distributed source.

-> Laboratory experiments with less volatile candidate species are ongoing and coma-modelling is planned.

Thank you for reading☺
Looking foreward to many interesting questions!