Thermal reactivity of HCN and NH_3 in interstellar ices.

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Introduction

- HCN is the simplest molecule containing the CN moiety, vital in the formation of amino acids and their precursors.[1] HCN has been observed extensively towards comets,[2] and is the major source of the abundant $CN^{\bullet}$ radical.[3]
- NH_3 is the most abundant basic molecular species in interstellar ices, at abundances of 2 - 15 % H_2O.[4]
- These species react to form a salt via:
  $HCN + NH_3 \rightarrow NH_4^+CN^-$
- Salt species are typically refractory, thus are present on the surface of dust grains at higher temperatures (> 150 K) to take place in a water-free chemistry.
- NH_4^+ is considered a likely candidate[5] to account for the unidentified 6.85 μm band observed towards YSOs[6,7] and quiescent regions.[8]
- The desorption characteristics of the product, the activation energy and rate of the reaction, and the infrared band strength of the CN^- ion were determined experimentally.

Experimental

- Experiments were carried out on the Reactivity on INterstellar Grains (RING, Fig 1.) set-up in the PIIM laboratory at Aix-Marseille Univ.
- HCN and NH_3 were prepared in separate mixing lines and co-deposited onto the gold surface, held at 10 K.

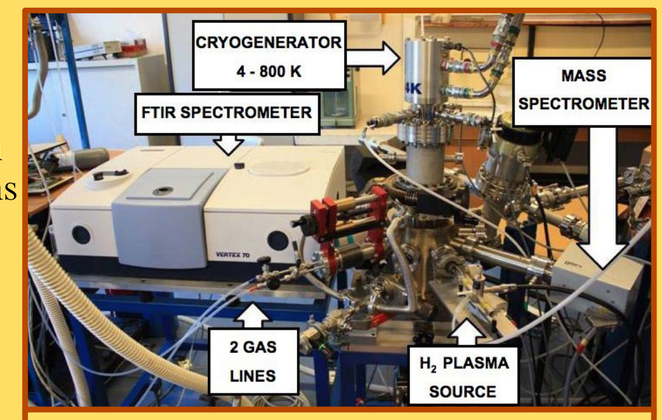

Fig 1. The RING experimental set-up at Aix-Marseille Université.

Infrared spectra and desorption characteristics

- A 1:5 HCN:NH_3 mixture was heated at 2 $Kmin^{-1}$ from 10 - 180 K.

The evolution of the ice was followed using FTIR spectroscopy (Fig 2) and the desorption by mass spectrometry (Fig 5).

Reaction Rate

- A series of ~1:15 HCN:NH_3 mixtures were investigated using the isotherm technique. Each mixture was heated quickly to a set temperature (between 60 - 105 K) and held at that temperature for a period of several hours (Fig 3 & 4). Ices were monitored using FTIR spectroscopy.

Salt Product

- $NH_4^+CN^-$ has distinctive bands at 1435 cm^{-1} (NH bend) and 2092 cm^{-1} (CN stretch).

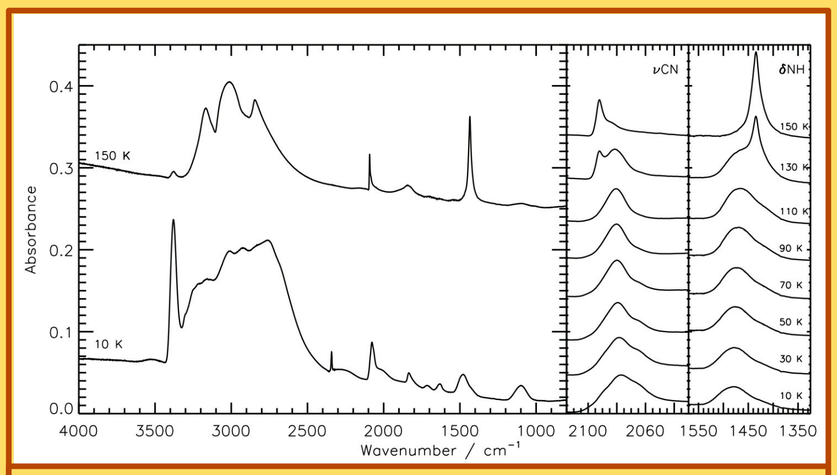

Fig 2. IR spectra of a 1:5 HCN: NH_3 mixture at 10 K, and after heating to 150 K. The CN stretching mode of HCN/CN^- and the NH bending mode of NH_4^+ are highlighted on the right.

- The band strength of the CN^- ion stretching mode absorption at 2092 cm^{-1} was determined to be: 1.8 ± 1.5 x 10^{-17} cm $molec^{-1}$ in the range 20 - 140 K.

Reaction rate

- Calculated to be: $k(T) = 0.016\ s^{-1} \exp(-2.7 \pm 0.4\ kJ\ mol^{-1} / RT)$

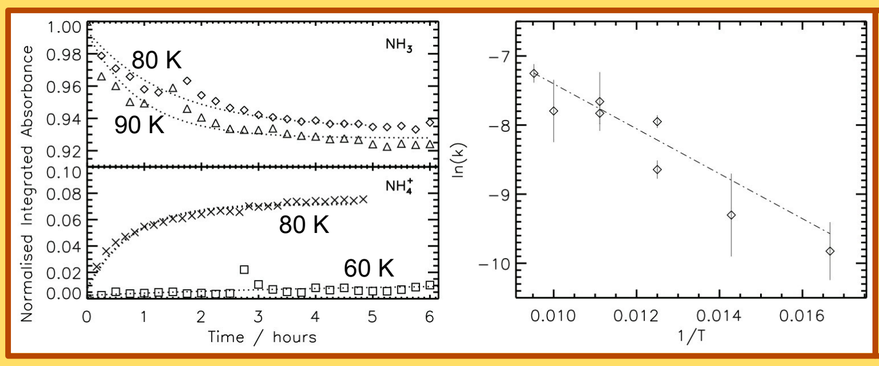

Fig 3. Time evolution of the normalised abundances of NH_3 and NH_4^+ at different fixed temperatures. The fits to the curves provide k(T) values.
Fig 4. The calculated k(T) values plotted as ln(k) vs 1/T. The kinetic parameters of the temperature-dependent reaction rate are determined by an Arrhenius law fitted to these data.

Desorption characteristics

- The desorption of $NH_4^+CN^-$ has an activation energy of 38.0 ± 1.4 kJ mol^{-1} with a pre-exponential factor of 10^{28} molec cm^{-2} s^{-1}.

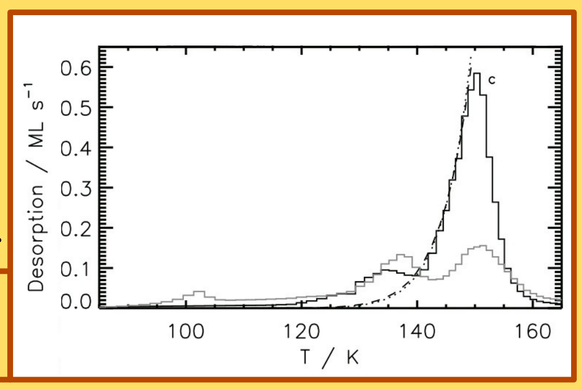

Fig 5. Temperature-programmed desorption spectra of m/z 27 (black) and 17 (grey) for the desorption of $NH_4^+CN^-$. The best-fitting zeroth order desorption kinetics are overplotted on m/z 27.

Astrophysical Implications

- Given the low predicted abundance of solid HCN ($10^{-7/-8}$ in gas phase,[9] thus 10^{-4} in solid phase), coupled with the low band strengths of HCN and CN^-, neither species can be observed with current IR telescopes.
- HCN chemistry gives rise to complex products, via $NH_4^+CN^-$, as illustrated in Fig 6.
- The formation of complex molecules such as polymers and salts allows the storage of simple species on grain surfaces at higher temperatures. Such molecules are able to take part in a water-free chemistry and are present in the organic residues on comets and meteorites.

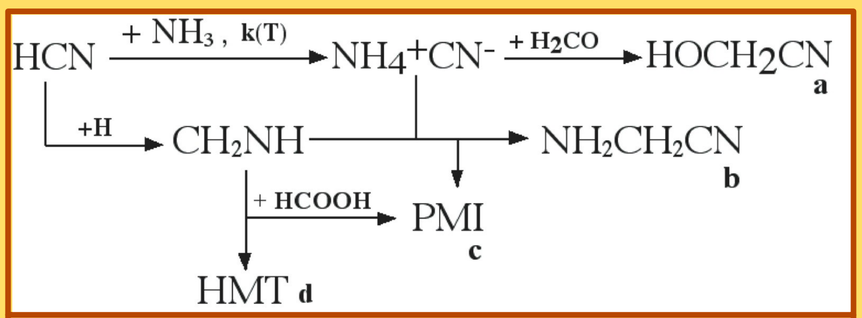

Fig 6. Simplified chemical network surrounding the thermal reaction product $NH_4^+CN^-$. The final products are a) hydroxyacetonitrile[10] ($HOCH_2CN$), b) aminoacetonitrile[1] (NH_2CH_2CN), c) poly(methylene-imine)[1] ($R\text{-}(CH_2\text{-}NH)_n\text{-}H$, where R= HCOO or CN), d) hexamethylenetetramine[11] ($C_6H_{12}N_4$).

References & Acknowledgements [1] Danger, G., Borget, F., Chomat, M., et al. 2011, A&A, 535, A47 [2] Bockelee-Morvan, D., Crovisier, J., Despois, D., et al. 1987, A&A, 180, 253 [3] Paganini, L., Villanueva, G. L., Lara, L. M., et al. 2010, ApJ, 715, 1258 [4] Bottinelli, S., Boogert, A. C. A., Bouwman, J., et al. 2010, ApJ, 718, 1100 [5] Schutte, W. A., & Khanna, R. K. 2003, A&A, 398, 1049 [6] Keane, J. V., Tielens, A. G. G. M., Boogert, A. C. A., Schutte, W. A., & Whittet, D. C. B. 2001, A&A, 376, 254 [7] Boogert, A. C. A., Pontoppidan, K. M., Knez, C., et al. 2008, ApJ, 678, 985 [8] Boogert, A. C. A., Huard, T. L., Cook, A. M., et al. 2011, ApJ, 729, 92 [9] Vasyunina, T., Linz, H., Henning, T., et al. 2011, A&A, 527, A88 [10] Danger, G., Duvernay, F., Theule, P., Borget, F., & Chiavassa, T. 2012, ApJ, 756, 11 [11] Vinogradoff, V., Duvernay, F., Danger, G., Theule, P., & Chiavassa, T. 2011, A&A, 530, A128.

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