*Conditions and Impact of Star Formation*
*R. Simon, R. Schaaf, and J. Stutzki (eds)*
*EAS Publications Series, Vol.* **75-76** *(2015) 315-320*



# CHEMICAL COMPLEXITY IN PROTOPLANETARY DISKS IN THE ERA OF ALMA AND ROSETTA

Catherine Walsh[1]

**Abstract.** Comets provide a unique insight into the molecular composition and complexity of the material in the primordial solar nebula. Recent results from the *Rosetta* mission, currently monitoring comet 67P/Churyumov-Gerasimenko *in situ*, and ALMA (the Atacama Large Millimeter/submillimeter Array) have demonstrated a tantalising link between the chemical complexity now confirmed in disks (via the detection of gas-phase $CH_3CN$; Öberg *et al.* 2015) and that confirmed on the surface of 67P (Goesmann *et al.* 2015), raising questions concerning the chemical origin of such species (cloud or inheritance versus disk synthesis). Results from an astrochemical model of a protoplanetary disk are presented in which complex chemistry is included and in which it is assumed that simple ices only are inherited from the parent molecular cloud. The model results show good agreement with the abundances of several COMs observed on the surface of 67P with *Philae*/COSAC. Cosmic-ray and X-ray-induced photoprocessing of predominantly simple ices inherited by the protoplanetary disk is sufficient to generate a chemical complexity similar to that observed in comets. This indicates that the icy COMs detected on the surface of 67P may have a disk origin. The results also show that gas-phase $CH_3CN$ is abundant in the inner warm disk atmosphere where hot gas-phase chemistry dominates and potentially erases the ice chemical signature. Hence, $CH_3CN$ may not be an unambiguous tracer of the complex organic ice reservoir. However, a better understanding of the hot gas-phase chemistry of $CH_3CN$ is needed to confirm this preliminary conclusion.

## 1 Probing ices in protoplanetary disks

Protoplanetary disks are the reservoirs of the basic components - dust, gas, and ice - required for the formation of planetary systems. The molecular components of midplane ices, in particular, sets the initial composition of icy planetesimals which

[1] Leiden Observatory, Leiden University, P. O. Box 9513, 2300 RA Leiden, The Netherlands


DOI: 10.1051/eas/1575063

can coalesce to form comets, and/or become swept up by forming planets. The chemical heritage of this icy planet- and comet-building material is much debated. Theories range from inheritance from the parent molecular cloud, chemistry en route from protostellar envelope to protoplanetary disk, to chemical processing within the protoplanetary disk once formed. Related to this is the origin of chemical complexity in planetary systems. The formation of many saturated (or close to saturated) organic molecules (*v.g.*, $CH_3OH$) is thought to occur on or within icy mantles on dust grains. Such species are considered an important bridge between the simple molecules generally detected in space, and those considered important for prebiotic chemistry, *v.g.*, amino acids.

It remains challenging to directly observe the icy planet-building material in protoplanetary disks (with the exception of water ice; *v.g.*, Pontoppidan *et al.* 2010; Terada *et al.* 2007; McClure *et al.* 2015). However, once the ice reservoir is released from the dust grains, either via heating (thermal desorption) or triggered by the absorption of energetic photons or particles (non-thermal desorption) the composition can be indirectly probed by gas-phase observations. Several of the expected dominant ice components (*v.g.*, $H_2O$, $CO_2$, CO, and $CH_4$) have been detected in the gas-phase in the warm/hot ($\gtrsim$ 300 K, $\lesssim$ 10 AU) inner regions of protoplanetary disks (*v.g.*, Carr & Najita 2008; Gibb & Horne 2013; Lahuis *et al.* 2006; Mandell *et al.* 2012). However, such observations probe the disk upper layers only and may reveal a composition different to that in the disk midplane within which the bulk of the planet-building reservoir resides (*v.g.*, Walsh *et al.* 2015). The indirect detection of the outer ($\gtrsim$ 10 AU) ice reservoir is more challenging. Here, non-volatile species (*v.g.*, $H_2O$) are thought to be desorbed non-thermally by UV photons from the central star and/or interstellar medium and are predicted to reside in a narrow layer bounded above by photodissociation and below by freezeout. Non-thermal desorption is less efficient than thermal desorption and so the peak abundances reached in the outer regions are orders of magnitude less than expected in the thermally desorbed regions. The first detection of cold water vapour in a protoplanetary disk with *Herschel* supports this picture (Hogerheijde *et al.* 2011).

COMs (loosely defined as consisting of 6 or more atoms; Herbst & van Dishoeck 2009) have a similar volatility as water and the additional challenge of intrinsically weaker emission arising from their inherent molecular complexity and typically lower abundances. Hence, very high sensitivity observations are required to detect emission from such gas-phase species, especially from small sources which span a few arcseconds only on the sky (such as protoplanetary disks). Luckily, we are now in the era of ALMA which has increased the achievable sensitivity of (sub)mm observations by several orders of magnitude. Indeed, Öberg *et al.* (2015) recently report the ALMA detection of a complex molecule, $CH_3CN$, in a protoplanetary disk (MWC 480) for the first time. Öberg *et al.* (2015) derive an abundance ratio for $CH_3CN$/HCN between $\approx$ 5% and 20% in line with that detected towards cometary comae ($\approx$ 10%; Mumma & Charnley 2011) suggesting that the emission arises from thermal desorption of the comet-building ice reservoir.

In parallel, the Rosetta mission is monitoring the chemical composition of 67P *in situ*. The COSAC (COmetary SAmpling and Composition) experiment on board the lander, *Philae*, has revealed a plethora of sub-surface COMs, including $CH_3CN$, $NH_2CHO$, $CH_3COCH_3$, and $CH_3OCN$, amongst others (Goesmann *et al.* 2015). The $CH_3CN$/HCN ratio measured with COSAC ($\approx 30\%$) is very similar to that observed in the disk around MWC 480 (Öberg *et al.* 2015).

In light of these new quantitative results from ALMA and *Rosetta*, I revisit the models presented in Walsh *et al.* (2014) which compute the abundance and distribution of COMs in a protoplanetary disk around a T Tauri star. One of the aims of these models was to test whether surface chemistry is able to efficiently synthesise COMs in protoplanetary disks given that the disk inherits only simple ices ($H_2O$, $CO_2$, CO, $N_2$, $CH_4$, $NH_3$, and $CH_3OH$). In Sect. 2 I discuss the abundance and distribution of $CH_3CN$ gas and ice, and in Sect. 3 I discuss the predicted abundances of those icy complex molecules detected in the sub-surface layers of 67P. I end with a short summary and future outlook (Sect. 4).

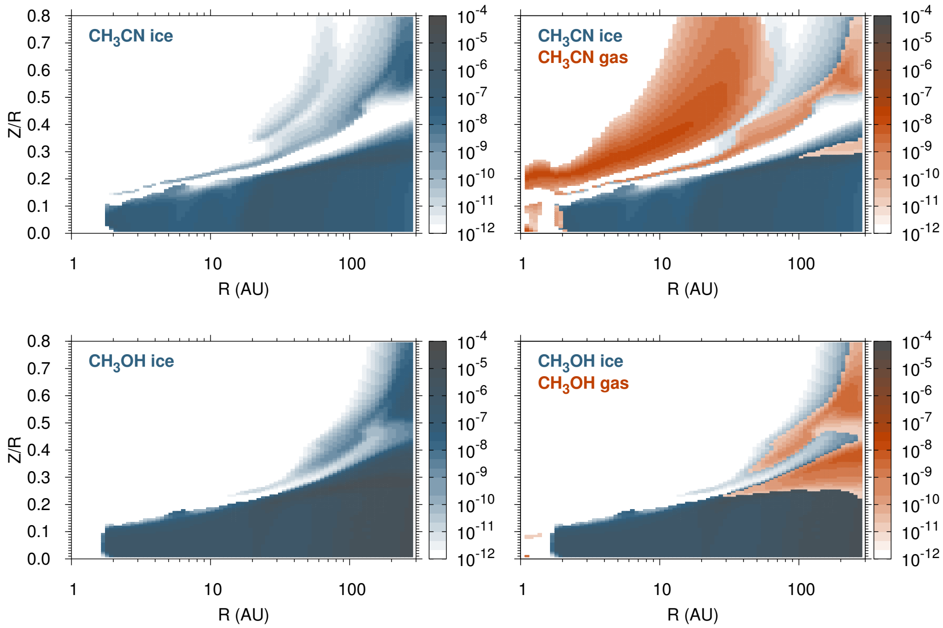
## 2 $CH_3CN$ gas in protoplanetary disks

In Fig. 1 I display the fractional abundance (relative to $H_2$) of $CH_3CN$ (top row) and $CH_3OH$ (bottom row) gas (orange) and ice (blue), as a function of disk radius and height. The physical conditions are those for an irradiated disk in hydrostatic equilibrium around a typical T Tauri star, and the chemical network includes gas-phase chemistry, gas-grain interactions, and grain-surface chemistry (see Nomura *et al.* 2007 and Walsh *et al.* 2014 for full details). $CH_3CN$ and $CH_3OH$ ice show a similar distribution with the complex ices reaching their peak abundance ($\sim 10^{-6}-10^{-5}$ relative to $H_2$, respectively) towards the disk midplane and towards the outer regions of the disk. As a comparison, water ice has a peak abundance a few times $10^{-4}$ relative to $H_2$. $CH_3CN$ gas has two reservoirs, a "hot" reservoir in the inner disk atmosphere within $\approx$ 30 AU and a narrow photodesorbed layer in outer disk tracing the boundary of the $CH_3CN$ ice layer. In contrast, $CH_3OH$ gas has an outer photodesorbed layer only. In the inner warm disk atmosphere, the chemical abundances are mediated by formation via gas-phase chemistry and/or desorption of the ice reservoir and destruction by gas-phase chemistry and photodissociation by the stellar radiation field. The results show that $CH_3CN$ gas can survive where $CH_3OH$ gas cannot, which potentially points to an efficient gas-phase formation route to $CH_3CN$, *i.e.*, $CH_3CN$ is not solely reliant on grain-surface synthesis, in contrast with $CH_3OH$ (as also discussed in Öberg *et al.* 2015). An alternative explanation is that the models are lacking destruction mechanisms for gas-phase $CH_3CN$. The results show that $CH_3CN$ in the inner regions of protoplanetary disks may not be directly tracing the composition of the comet-forming zone; however, a better understanding of the gas-phase chemistry of $CH_3CN$ in the inner warm regions of protoplanetary disks is required to confirm this preliminary conclusion.

## 3 Icy complex molecules in the comet-forming zone

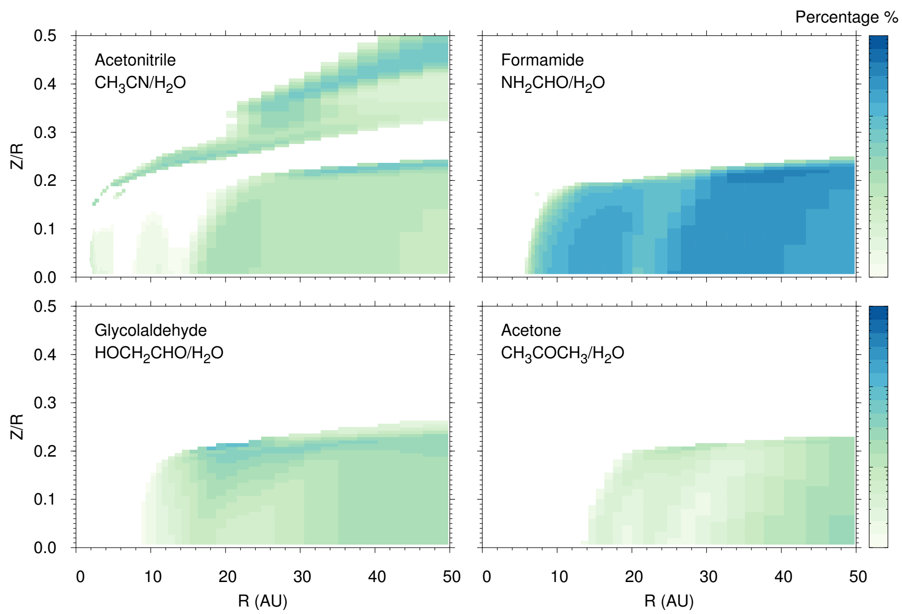
In Fig. 2 I display the ice abundances of four complex molecules calculated using the same disk model ($CH_3NH_2$, $NH_2CHO$, $HOCH_2CHO$, and $CH_3COCH_3$).

**Fig. 1.** Abundance of $CH_3CN$ gas (orange) and ice (blue) relative to $H_2$ (top row) as a function of disk radius, $R$, and height (scaled by the radius, $Z/R$), compared with the same data for $CH_3OH$ gas and ice (bottom row). Data are from Walsh *et al.* (2014).




These species have all been detected in the *Philae*/COSAC measurements of the sub-surface composition of 67P (Goesmann *et al.* 2015). The abundances are presented as a percentage relative to water ice in the disk and the data plotted are restricted to within the comet-forming zone ($\leq$ 50 AU). The results show that chemical processing within the disk is able to efficiently convert the initial simple ices to more complex species. The key process is photodissociation of ice species by UV photons generated by the interaction of galactic cosmic rays and stellar X-rays with molecular hydrogen. This creates a local source of reactive radicals in the ice mantle to increase complexity. Despite a generic model being adopted, the abundances of the four ice species presented show remarkable agreement with the ratios derived from the *Philae*/COSAC measurements (0.3% for $CH_3CN$, 1.5% for $NH_2CHO$, 0.4% for $HOCH_2CHO$, and 0.3% for $CH_3COCH_3$). The model results also show good agreement with the observations for $CH_3CHO$; however, HNCO and $CH_3NH_2$ are underpredicted and overpredicted, respectively. The reason for this may be because both HNCO and $CH_3NH_2$ are products formed during successive hydrogenation of OCN and HCN. In both cases, the hydrogenation pathways used in the models may be too efficient, although the latter has been demonstrated in the laboratory (Theulé *et al.* 2011). Conversely, recent laboratory experiments

**Fig. 2.** Percentage of $CH_3CN$, $NH_2CHO$, $HOCH_2CHO$, and $CH_3COCH_3$ ice relative to water ice, as a function of disk radius, $R$, and height (scaled by the radius, $Z/R$). Data are from Walsh *et al.* (2014).




on hydrogenation of HNCO ice have shown that hydrogenation does not always lead to saturation (Noble *et al.* 2015).

The models also do not reproduce the relative abundances of $HOCH_2CH_2COH$, $C_2H_5CHO$, and $C_2H_5NH_2$ observed with *Philae*/COSAC because the network employed has limited chemistry for these larger species. Chemical networks, including the one employed here, also do not yet include chemistry for $CH_3OCN$, neither in the gas phase nor in the ice. In light of these exciting results from *Philae*/COSAC, the expansion of surface networks to better treat these larger species should be undertaken including potential pathways to the larger COMs mentioned above, which have been demonstrated in the laboratory but not yet considered in the models (*v.g.*, for $HOCH_2CH_2COH$; Fedoseev *et al.* 2015).

## 4 Discussion and future outlook

The model results show that COMs can be efficiently synthesised via surface chemistry in the cold, dense midplanes of protoplanetary disks, assuming that the disk inherits simple ices only from the parent molecular cloud. The abundances attained for several species in the comet-forming regions ($\lesssim$ 50 AU) are on a par with those recently observed on 67P. The vital chemical process is cosmic-ray and

X-ray-induced photodissociation of ice mantle molecules. This allows the processing of icy material in the cold dense midplane which is otherwise well shielded from both stellar and interstellar UV photons. The result for gas-phase $CH_3CN$ suggest that this species may not be an unambiguous tracer of the ice reservoir in the inner regions of disks; however, a better understanding of the gas-phase chemistry of $CH_3CN$ under these particular physical conditions is required to confirm this conclusion. Gas-phase $CH_3OH$, yet to be detected in a protoplanetary disk, may be a more robust tracer of the complex ice reservoir.

The observational results discussed here give a tantalising hint of what is to come in the near future. The first detection of a complex molecule in a protoplanetary disk with ALMA gives the community vital information on the sensitivities required to detect these heretofore elusive species, that will surely be exploited in future cycles. In addition, a small fraction only of the data from *Rosetta* has been published to date, with much more to come. Furthermore, a new era of infrared astronomy approaches, with MIRI (Mid-InfraRed Instrument) on JWST (James Webb Space Telescope, to be launched in 2018) providing unparalleled spectral resolution and sensitivity from 5 to 28 $\mu$m (Wright *et al.* 2004). MIRI is expected to have the sensitivity necessary to observe the infrared signature of ice species other than water in protoplanetary disks for the first time, which may provide the first *direct* detection of the complex organic reservoir in these objects.

## References

Carr, J. S. & Najita, J. R. 2008, Science, 319, 1504
Gibb, E. L. & Horne, D. 2013, ApJ, 776, L28
Goesmann, F., Rosenbauer, H., Bredehöft, J. H., *et al.* 2015, Science, 349, 689
Fedoseev, G., Cuppen, I., Ioppolo, S., *et al.* 2015, MNRAS, 448, 1288
Herbst, E. & van Dishoeck, E. F. 2009, ARA&A, 47, 427
Hogerheijde M. R., Bergin, E. A., Brinch, C., *et al.* 2011, Science, 334, 338
Lahuis, F., van Dishoeck, E. F., Boogert, A. C. A., *et al.* 2006, ApJ, 636, L145
Mandell, A. M., Bast, J., van Dishoeck, E. F., *et al.* 2012, ApJ, 747, 92
McClure, M. K., Espallait, C., Calvet, N., *et al.* 2012, ApJ, 799, 162
Mumma, M. J. & Charnley, S. B. 2011, ARA&A, 49, 471
Noble, J. A., Theulé, P., Congiu, E., *et al.* 2015, A&A, 576, A91
Nomura, H., Aikawa, Y., Tsujimoto, M., *et al.* 2007, ApJ, 661, 334
Öberg, K. I., Guzmán, V. V., Furuya, K., *et al.* 2015, Nature, 520, 198
Pontoppidan, K. M., Dullemond, C. P., van Dishoeck, E. F., *et al.* . 2005, ApJ, 622, 463
Terada, H., Tokunaga, A. T. Kobayashi, N., *et al.* 2007, ApJ, 667, 303
Theulé, P., Borget, F., Mispelaer, F., *et al.* . 2011, A&A, 534, A64
Walsh, C., Millar, T. J., Nomura, H., *et al.* 2014, A&A, 563, A33
Walsh, C., Nomura, H., & van Dishoeck, E. F. 2015, A&A, 582, A88
Wright, G. S., Reike, G. H., Colina, L., *et al.* 2004, SPIE, 5487, 653