Questions about the evolution of ices, from diffuse molecular clouds to comets

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Abstract. The surfaces of interstellar and circumstellar dust grains are the sites of molecule formation, most of which, except H_2, stick and form ice mantles. The study of ice evolution thus seems directly relevant for understanding our own origins, although the relation between interstellar and solar system ices remains a key question. The comparison of interstellar and solar system ices relies evidently on an accurate understanding of the composition and processes in both environments. With the accurate *in situ* measurements available for the comet 67P/Churyumov-Gerasimenko with the Rosetta mission, improving our understanding of interstellar ices is the more important. Here, I will address three specific questions. First, while laboratory experiments have made much progress in understanding complex organic molecule (COM) formation in the ices, the question remains, how does COM formation depend on environment and time? Second, what is the carrier of sulfur in the ices? And third, can ice absorption bands trace the processing history of the ices? Laboratory experiments, ranging from infrared spectroscopy to identify interstellar ice species, to surface experiments to determine reaction parameters in ice formation scenarios, to heating and irradiation experiments to simulate space environments, are essential to address these questions and analyze the flood of new observational data that will become available with new facilities in the next 2-10 years.

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1. Introduction

The evolutionary sequence from diffuse† to dense molecular clouds and protostellar envelopes, and protoplanetay disks, is governed by the physical processes of turbulence, shocks, radiation, and gravitational collapse and accompanied by an impressive chemical evolution. Increasing densities shield the dust grains from the interstellar radiation field, leading to the formation of icy mantles on refractory dust grains. Telescope observations, analyzed using laboratory-measured ice spectra, have revealed that the icy mantles consist of layers dominated by H_2O and CO (see review by Boogert *et al.* 2015). Each layer is a complex mixture of simple molecules, with H_2O mixed with CO_2, CH_4, and NH_3 formed early in the cloud evolution, while CO can be pure or mixed with CH_3OH and OCN^- and is formed later, at higher densities. The observations have raised important questions that directly relate to the interstellar ices as a reservoir for the formation of planetary system ices. Here I touch upon three questions. First, while laboratory experiments have made much progress in understanding complex organic molecule (COM) formation in the ices, the question remains, how does COM formation depend on environment and time? Second, what is the carrier of sulfur in the ices? And third, can ice absorption bands trace the processing history of the ices? New facilities coming online

† diffuse molecular clouds refers to clouds with $A_V > 0.2$ (Snow & McCall 2006)

in the next years, in particular, JWST (James Webb Space Telescope) and SPHEREx (Spectro-Photometer for the History of the Universe, Epoch of Reionization, and Ices Explorer) are expected to provide important new observational constraints, and the goal of these conference proceedings is to show that continued investment in laboratory ice experiments is warranted.

2. How does complex organic molecule formation depend on environment and time?

The onset of ice formation can be determined by measuring the ice formation threshold, which is the cloud depth at which ice formation takes off, typically expressed in magnitudes of visual extinction A_V. Different thresholds are observed for different species, reflecting differences in condensation temperatures, photodesorption yields, and chemical reaction efficiencies, all of which are being measured in laboratories and used in astrochemical models. For H_2O, CO_2, and CO, these thresholds are quite well understood (e.g., Hollenbach *et al.* 2009), but for CH_3OH the situation is less clear. H_2O and CO_2 ice form at a depth of ~ 1.6 mag into dense clouds, reflecting OH formation from atomic H and O, which subsequently forms H_2O and CO_2 (from CO+OH). At a depth of ~ 3 mag, CO ice is observed. But, CO, being very volatile, only freezes out completely deeper into the cloud, at higher densities and lower temperatures. At this point, large gas phase H/CO ratios are optimal to hydrogenate CO ice and form H_2CO and CH_3OH (Cuppen *et al.* 2009). Above $A_V \sim 9 \pm 3$ mag, CH_3OH ice abundances have been observed at the 10% level relative to H_2O ice. This behavior is not universal, however, as many lines of sight with A_V values well above 9 mag show much lower CH_3OH ice abundances (Boogert *et al.* 2011). Clearly, A_V is not the only parameter that determines CH_3OH ice formation. Presumably, and not surprisingly, local physical conditions (densities and temperatures) or time scales, are most relevant.

2.1. *The need for ice mapping*

Understanding the large variations of the CH_3OH ice abundance is a key issue in astrochemistry, because this species is a prime precursor or indicator of COM formation, either by grain surface reactions (Fedoseev *et al.* 2015), or by energetic processing (Gerakines *et al.* 1996). Thus it is a prime observational goal to relate local physical conditions to abundances of CH_3OH ice, as well as its precursors H_2CO and CO, and other CO derivatives, in particular CO_2 and OCN^-. Indeed, abundance maps as well as absorption profile variations of these ice species in molecular clouds should be correlated with maps of dust and gas temperature and density derived by millimeter-wave observations. The ice maps have to be constructed using infrared absorption spectroscopy of stars behind molecular clouds. Current maps are of poor quality due to a lack of suited instrumentation. State-of-the-art CH_3OH ice "maps" are limited to a few sight-lines per cloud (Boogert *et al.* 2011; Fig. 1). The best CH_3OH ice map is that tracing the envelope of a Class 0 protostar (Pontoppidan *et al.* 2004).

The lack of ice maps is the result of an unfortunate mismatch of either spectral resolving power and wavelength coverage (Spitzer Space Telescope) or sensitivity (Infrared Space Observatory, ground-based telescopes). Fortunately, the upcoming mission James Webb Space Telescope (JWST) has all the capabilities needed for constructing ice maps (resolving power of a few 1000, multi-object modes, high sensitivity, large wavelength coverage). It is expected to be launched in March 2021. One of the approved thirteen Early Release Science programs, called "Ice Age" (McClure *et al.* 2017) will guarantee that an ice map will be obtained in the first year of the mission. Later in the JWST mission, a larger sample of ice maps should be obtained. The target selection for JWST
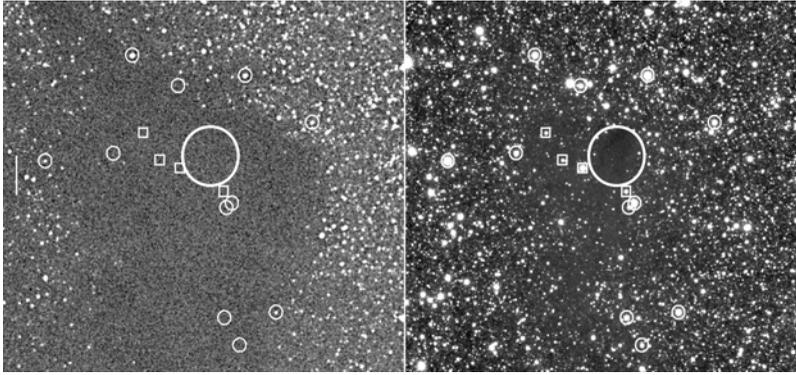
Figure 1. UKSTU "Red" optical (left) and K-band CTIO-4m/ISPI images (right), of the 11×9.5 arcmin^2 region around the isolated dense core L429-c. A scale of 1 arcmin is represented by the white bar at the left. The four targets with confirmed CH$_3$OH ice detections (Boogert *et al.* 2011) are marked by squares, and have $A_V > 30$ mag. The small circles are for background stars being targeted by an ongoing observing program. Towards the edge of the image, A_V is about 1 mag. The large circle indicates a very dense region ($A_V > 100$), likely in an initial collapse phase (Stutz *et al.* 2009). JWST will be able to map the ices in such cores much more efficiently, at high sensitivity, resolution, and spectral coverage, and thus trace the formation conditions of a range of molecules.

will be improved by the all sky 0.7-5 μm maps obtained (at low spectral and spatial resolution) with SPHEREx (Doré *et al.* 2016), a mission approved to be launched in 2023.

2.2. *Observing icy COMs*

Laboratory experiments have convincingly shown that the processing of CH$_3$OH-containing ices by ultraviolet photons, cosmic rays, and heat, leads to COMs (e.g., Gerakines *et al.* 1996). But surface chemistry experiments have proven that complexity can also be achieved under cold, non-energetic conditions (e.g., Fedoseev *et al.* 2015; for a review also see Linnartz *et al.* 2015) by a combination of addition and abstraction reactions with CO as a starting point. The direct identification of these COMs in interstellar ices is fundamentally limited, because infrared spectroscopy traces the vibrational modes of molecular groups, not specific molecular species. Still, poorly identified interstellar ice absorption features do exist, e.g., at 7.2, 7.4, and 7.6 μm, and could be due to COMs, although still the simplest ones (e.g., CH$_3$CH$_2$OH, CH$_3$CHO). Improved constraints on their origin can be expected if the number of sight-lines in which these features are detected increases from just a few at present to at least tens in the JWST-era, in well resolved spectra. It will then be possible to correlate the absorption profiles and relative depths with environmental characteristics, such as temperature, density, radiation fields, and time scales. To prepare for this, laboratory spectroscopy of frozen COMs as a function of molecular environment and temperature is under way (Terwisscha van Scheltinga *et al.* 2018, poster by Rachid *et al.*, see page 420).

2.3. *CH$_3$OH formation at low* A_V

Ices likely exist on the dust grains below the ice formation threshold, but defy detection due to the sensitivity limits of infrared spectroscopy. It is thus more correct to refer to the ice formation thresholds as the depth into molecular clouds at which the ice abundance increases rapidly. A small CH$_3$OH reservoir may be expected from CO hydrogenation

below the observed threshold of $A_V = 9\pm3$ mag, yet has not been detected to the level of a few percent relative to H_2O ice. Other CH_3OH formation routes are likely at play at these low A_V's as well. Indeed, laboratory experiments by Qasim *et al.* (2018) found that the abstraction reaction of $CH_4 + OH$ leading to CH_3 and H_2O, followed by $CH_3 + OH$ will form CH_3OH in the ices. Considering that the CH_4 ice abundance is more than an order of magnitude smaller than that that of CO, a correspondingly small amount of CH_3OH is expected to form this way. Cloud edges, however, at A_V values of a few mag, tentatively show CH_4/H_2O ratios that are enhanced by a factor of two (Öberg *et al.* 2011) due to the incomplete formation of gas phase CO. And there may well be other CH_3OH formation routes. A quantitative assessment of the formation of CH_3OH at low A_V is still needed. Note that a low, undetectable CH_3OH ice abundance of, say, 0.1% relative to H_2O corresponds to $\sim 10^{-7}$ relative to H_2, which is comparable to or (much) larger than the abundances of many gas phase species in hot molecular cores (e.g., CN, CS, HC_3N, H_2CO; Blake *et al.* 1987).

3. What is the carrier of sulfur in the ices?

Sulfur chemistry in dense clouds and protostellar environments is not well constrained, because observations have identified only a fraction of the cosmic budget for this element. Both dust and ices may well harbor large reservoirs of sulfur. Frozen OCS, and perhaps SO_2, lock up at most 4% of the cosmic sulfur budget. Gas phase spectroscopy provides an alternative, indirect measurement of the ice composition. Millimeter-wave spectroscopy, in particular with ALMA, is in fact orders of magnitude more sensitive to molecular abundances. Gas phase infrared absorption spectroscopy traces all gas against the continuum emission by hot dust surrounding the protostar, unaffected by beam dilution, and also gives access to molecules without permanent dipole moment. We are therefore performing a high spectral resolution infrared (3-14 μm) gas phase line survey of hot molecular cores surrounding massive protostars using ground-based (IRTF/iSHELL, IRTF/TEXES, Gemini/TEXES) and airborne (SOFIA/EXES) instruments. One readily detected species in this survey is CS (Barr *et al.* 2018). It is located in hot ($\sim$700 K) gas close ($<$ 130 AU) to the central star, and locks up $\sim$6% of the sulfur towards the massive hot core AFGL 2591, assuming standard conversion factors between the observed CO column density and H_2.

Towards another hot core, Mon R2 IRS3, a similar amount of sulfur is locked up in gas phase SO_2 (Dungee *et al.* 2018). Very narrow absorption lines ($FWHM <$5 km/s) were linked to the release of sulfur from sublimated ices, rather than sputtering from refractory grains in shocks. The question remains what this ice species is. The SO_2 ice, tentatively observed towards massive protostellar envelopes, has an abundance relative to H_2O of just 0.5%, while in the gas it is $\sim$10%. Many chemical models assume an efficient formation of H_2S in the ices, analogous to H_2O formation. The sublimated H_2S would then convert to SO and SO_2 by gas phase reactions in the hot core (Charnley *et al.* 1997). A key question here is the H_2S ice abundance. An upper limit to the H_2S/H_2O ice abundance ratio of 1.1% (Smith 1991) is inconsistent with the gas phase SO_2/H_2O ratio of 10%. *in situ* measurements of the sulfur abundances in the comet 67P/Churyumov-Gerasimenko, on the other hand, show that indeed H_2S is the most abundant sulfur carrier (Calmonte *et al.* 2016), followed by sulfur allotropes. Dungee *et al.* (2018) thus suggest allotropes as a source for the observed large gas phase SO_2 abundance. But evidently, the inconsistency of the H_2S ice abundances between these comet and dense cloud observations needs further investigation. Measurements of the H_2S, SO_2, and OCS ice abundances in interstellar and circumstellar ices are presently sparse, but will be investigated systematically with the JWST mission. Along with this, laboratory experiments should investigate the stability of H_2S in the ices (Palumbo *et al.* 1997 note that

H_2S is susceptible to H-abstraction reactions and that in fact SO_2 should be the most abundant sulfur-bearing ice species), as well as the formation efficiencies of other sulfur-bearing species. Laboratory ice spectroscopy is needed as well, and a program is currently underway (Hudson & Gerakines 2018).

4. Can ice absorption profiles trace the processing history of the ices?

The CO_2 ice absorption profiles have proven to be particularly powerful tracers of the interstellar and circumstellar ice composition and thermal history (e.g., Pontoppidan *et al.* 2008). Distinct profile changes for ices around YSOs have been attributed to the sublimation of CO in CO:CO_2 mixtures and, at higher temperature, to the segregation of CO_2 in H_2O:CO_2 mixtures at the amorphous to crystalline transition of H_2O ice. Indeed, as this phase transition is time-dependent at a given temperature, the CO_2 ice bands are tracers of the time scales of protostellar envelope heating. Recent laboratory experiments (He *et al.* 2018) put the usefulness of the CO_2 bands as time scale tracers into doubt, however. No segregation was observed at CO_2/H_2O ratios of less than 23%. It so happens that this number is within the range of column density ratios observed towards dense clouds and protostars (11-50%; Boogert *et al.* 2015). Thus, the absence of segregation signatures would not necessarily imply a lack of heating. This interpretation is complicated by the possibility that within the ice mantles, CO_2/H_2O ratios may vary. For example, early in the cloud evolution, the gas phase conversion of C to CO may not be complete, while H_2O ice formation is ongoing, leading to lower CO_2/H_2O ratios early on (but higher CH_4/H_2O ratios as tentatively found in Öberg *et al.* 2008), and thus higher CO_2/H_2O ratios in ice layers formed later for the same observed total column densities. As an alternative to the $^{12}CO_2$ band profiles (in particular the 15 μm bending mode), He *et al.* (2018) propose the $^{13}CO_2$ ice band at 4.39 μm as a good thermal history tracer. They find that the peak position and width of this band depend linearly on temperature, and not on concentration. This would require high signal-to-noise measurements of this weak band by the upcoming JWST mission. This method is also complicated by the interference by other ice components, e.g. CO mixed with CO_2, though a combined $^{12}CO_2$ and $^{13}CO_2$ band analysis may be able to mitigate this. Also, while this method can trace the thermal history, it cannot be translated into time scales.

5. Conclusions

I conclude that laboratory experiments lead the way in understanding the formation of COMs in the ices. Much-needed observational constraints will come after the launch of the JWST telescope. JWST will provide maps of CO, CO_2, CH_3OH, OCN^-, and H_2O toward diffuse and dense molecular clouds and protostellar envelopes. JWST will also provide deep searches for icy COMs in much larger samples than we have done so far. Constraints provided by current ground-based, airborne, and future JWST observations of gas and solid state sulfur-bearing species warrant laboratory experiments on their spectroscopic and chemical properties. This will enable a better comparison with the accurate *in situ* measurements of the ubiquitously present sulfur-bearing molecules in cometary ices, offering an interesting tool to trace the origin of primitive solar system materials. Finally, laboratory spectroscopy of CO_2:H_2O ices have shown that the use of these mixtures as tracers of the thermal history of the ices in future JWST observations is complicated by a dependency of ice segregation on the CO_2 concentration. Overall, laboratory experiments, ranging from infrared spectroscopy to identify interstellar ice species, to surface experiments to determine reaction parameters in ice formation scenarios, to heating and irradiation experiments to investigate evolutionary effects, are essential to

address critical questions in astrochemistry and analyze the flood of new observational data that will become available with new facilities in the next 2-10 years

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