

On the origin of O₂ and other volatile species in comets

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Abstract. Molecular oxygen, O₂, was recently detected in comet 67P by the ROSINA instrument on board the Rosetta spacecraft with a surprisingly high abundance of 4% relative to H₂O, making O₂ the fourth most abundant in comet 67P. Other volatile species with similar volatility, such as molecular nitrogen N₂, were also detected by Rosetta, but with much lower abundances and much weaker correlations with water. Here, we investigate the chemical and physical origin of O₂ and other volatile species using the new constraints provided by Rosetta. We follow the chemical evolution during star formation with state-of-the-art astrochemical models applied to dynamical physical models by considering three origins: i) in dark clouds, ii) during forming protostellar disks, and iii) during luminosity outbursts in disks. The models presented here favour a dark cloud (or “primordial”) grain surface chemistry origin for volatile species in comets, albeit for dark clouds which are slightly warmer and denser than those usually considered as solar system progenitors.

Keywords. astrochemistry, comets: individual: 67P/C-G, ISM: abundances, ISM: molecules, protoplanetary discs, stars: formation

1. Introduction

The *Rosetta* spacecraft analysed the Jupiter-family comet 67P/Churyumov-Gerasimenko (hereinafter comet 67P/C-G) in 2014 and 2015. The ROSINA instrument on board the *Rosetta* orbiter (Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (Balsiger *et al.* 2007) detected a “zoo” of molecules in the coma of 67P/C-G from simple monoatomic or di-atomic species to complex pre-biotic molecules, such as glycine, the simplest amino-acid (Le Roy *et al.* 2015, Altwegg *et al.* 2016).

One of the most surprising results provided by the ROSINA instrument is the *in-situ* detection of molecular oxygen, O₂, in the coma of comet 67P/C-G, resulting in the first detection of O₂ in a comet (Bieler *et al.* 2015). O₂ is strongly correlated with H₂O and is present at an average level of $3.80 \pm 0.85\%$ relative to H₂O, making it the fourth most abundant molecule in the comet, following H₂O, CO₂, and CO. The authors argue that O₂ does not originate from gas-phase chemistry in the coma but from direct sublimation from or within the comet surface. Moreover, the strong correlation with H₂O suggests that the O₂ is trapped within the bulk H₂O ice matrix of the comet and therefore that O₂ was present within the ice mantle on dust grains in the presolar nebula prior to comet formation since the surface of comet 67P/C-G revealed today is likely pristine. A reanalysis of data from the Neutral Mass Spectrometer on board the *Giotto* probe which

did a fly-by of comet 1P/Halley in 1986, confirmed the presence of O₂ at a level similar to that seen in 67P/C-G (Rubin *et al.* 2015b). This suggests that O₂ is not only an abundant molecule in comets, but is also common to both Jupiter-family comets, such as 67P/C-G, and Oort Cloud comets, such as 1P/Halley, which have different dynamical behaviours and histories. These results raise the question whether O₂ was abundant in icy dust mantles entering the protoplanetary disk of the young Sun, or whether the conditions in the comet-forming zone of the early solar system were favourable for O₂ formation and survival.

O₂ is a diatomic homonuclear molecule; hence it does not possess electric dipole-allowed rotational transitions. Therefore, gas-phase O₂ has been particularly elusive in interstellar clouds. Recent high sensitivity observations with the *Herschel Space Observatory* allowed a deep search for O₂ towards sources considered as true solar system progenitors: low-mass protostars. A deep upper limit was determined towards the well-studied protostar, NGC 1333-IRAS 4A, (O₂/H₂ ≤ 6 × 10⁻⁹ or O₂/H₂O ≤ 0.012% with a H₂O abundance of ~ 5 × 10⁻⁵, Yildiz *et al.* 2013). This picture is consistent with laboratory experiments that have shown that O₂ ice is efficiently hydrogenated at low temperatures and converted into H₂O and H₂O₂ ices (Ioppolo *et al.* 2008, Miyachi *et al.* 2008). This makes the close association of O₂ with H₂O in 67P/C-G an even stronger enigma.

Despite O₂ being a particularly elusive molecule in interstellar and circumstellar environments, there apparently do exist conditions which are favourable for the formation of O₂ and related species at abundance ratios similar to that observed in ices in comet 67P/C-G. Indeed, *Herschel* did reveal the presence of gas-phase O₂ in two sources: an active star forming region in Orion (Goldsmith *et al.* 2011) and in the dense core ρ Oph A located in the more quiescent ρ Oph molecular cloud complex, which stands out from other low-mass star-forming regions by exhibiting emission from relatively warm molecular gas (Larsson *et al.* 2007, Liseau *et al.* 2012). Subsequent observations of ρ Oph A have also determined the presence of related gas-phase species, HO₂ and H₂O₂, at abundance levels in reasonable agreement with those seen in 67P/C-G with ROSINA (~ 2 × 10⁻³ that of O₂, see Bergman *et al.* 2011b, Parise *et al.* 2012). The chemically related species, O₃ (ozone), was not detected in the comet coma with a very low upper limit, < 2.5 × 10⁻⁵ with respect to O₂.

Other key di-atomic molecules of similar volatility, CO and N₂, have also been detected in 67P/C-G by *Rosetta* but with a much weaker correlation with H₂O (Rubin *et al.* 2015a, Bieler *et al.* 2015). Although CO shows a high abundance of 10-30% relative to H₂O, in good agreement with previous observations towards other comets, N₂ shows a much lower abundance of 0.57 ± 0.07 % relative to CO. The different correlations and abundances w.r.t. the H₂O clearly suggest a different chemical history for O₂, CO, and N₂.

Here we explore and discuss several different origins to explain the strong constraints provided by *Rosetta* on O₂ and other volatile species in comet 67P/C-G: i) in dark clouds (“primordial” origin), ii) during the journey from the protostellar envelope into the disk, iii) during luminosity outbursts within the protoplanetary disk.

2. Astrochemical models

The gas-grain astrochemical models by Taquet *et al.* (2014) and Furuya *et al.* (2015) have been used in this work to study the formation and survival of O₂ and other volatile species from dark clouds to the Solar System. These models couple the gas phase and ice chemistries with the approach developed by Hasegawa & Herbst (1993) to follow the multi-layer formation of interstellar ices and to determine the gas-ice balance. Several sets of differential equations, one for gas-phase species, one for surface ice-mantle species, and

one (or several) for bulk ice-mantle species, are considered to follow the time-evolution of abundances. Following Vasyunin & Herbst (2013), the chemically-active surface is limited to the top four monolayers. The original three-phase model considered in the Taquet model assumes that the inert bulk ice mantle has a uniform molecular composition. In order to accurately follow the ice evolution in warm conditions, the Furuya model considers a depth-dependent molecular composition, through the division of the inert bulk ice mantle into five distinct phases (for details, see Furuya *et al.* 2016 and references therein).

The gas-phase chemical network used by the Taquet model is based on the 2013 version of the KIDA chemical database (Wakelam *et al.* 2012). It has been further updated to include warm gas-phase chemistry involving water and ion-neutral reactions involving ozone. The network also includes the surface chemistry of all dominant ice components, as well as those important for water (e.g., O₂, O₃, and H₂O₂). Several new surface reactions were added involving O₃ and reactive species such as N, O, OH, NH₂, and CH₃, following the NIST gas-phase chemical database. The gas-ice chemical network of Garrod & Herbst (2006), based on the OSU 2006 network, is used in the Furuya model. The gas phase and surface networks in the Furuya model are more suited to the high density and warm temperatures conditions found in protostellar envelopes. It has therefore been supplemented with high-temperature gas-phase reactions from Harada *et al.* (2010) and includes the formation of many complex organic molecules. It is consequently more expansive than the network used in the Taquet model.

Elemental abundances of species used in the two models correspond to the set EA1 from Wakelam & Herbst (2008). Standard input parameters assumed for the two astrochemical models are: a cosmic ray ionisation rate ζ of $1 \times 10^{-17} \text{ s}^{-1}$, a flux of secondary UV photons of $10^4 \text{ phot. cm}^{-2} \text{ s}^{-1}$, a dust-to-gas mass ratio of 1%, a grain diameter of $0.2 \mu\text{m}$, a volumic mass of grains of 3 g cm^{-3} , a grain surface density of 10^{15} cm^{-2} , a diffusion-to-binding energy ratio of 0.5, four chemically active monolayers, and a sticking coefficient of species heavier than H and H₂ of 1.

3. Interstellar chemistry of molecular oxygen

Two main processes have been invoked for the formation of molecular oxygen in the interstellar medium: i) gas-phase formation via neutral-neutral chemistry, and ii) formation via association reactions on/within icy mantles of dust grains. Gaseous O₂ is thought to form primarily via the barrierless neutral-neutral reaction between O and OH in cold and warm gas. Due to its importance, this reaction has been well studied both experimentally and theoretically. The formation of O₂ in cold dark clouds is initiated by the high initial abundance assumed for atomic oxygen, inducing an efficient ion-neutral chemistry that also forms OH. In warm environments ($T \gtrsim 100 \text{ K}$), e.g., the inner regions of protostellar envelopes or the inner, warm layers of protoplanetary disks, OH and O are mostly produced through warm neutral-neutral chemistry driven by the photodissociation of water sublimated from interstellar ices. Solid O₂ in dark clouds is involved in the surface chemistry reaction network leading to the formation of water ice (Tielens & Hagen 1982, Miyauchi *et al.* 2008, Ioppolo *et al.* 2008). O₂ is formed through atomic O recombination on ices and efficiently reacts with either atomic O or atomic H to form O₃ or HO₂, respectively, eventually leading to the formation of water. The hydrogenation of O₃ also leads to the formation of O₂, in addition to dominating the destruction of O₃.

Radiolysis, i.e. the bombardment of (ionising) energetic particles depositing energy into the ice, and/or photolysis, i.e. the irradiation of ultraviolet photons breaking bonds, can trigger chemistry within the mantle of cold interstellar ices. We have investigated the

impact of the UV photolysis induced by secondary UV-photons on the bulk ice chemistry and the formation and survival of O₂. We find that O₂ cannot be efficiently produced in the bulk through ice photolysis as the photodissociation of the main ice components not only produces O atoms, that recombine together to form O₂, but also H atoms that react with O₂ to reform water. Laboratory experiments show that O₂ can be efficiently formed through radiolysis of ices without overproducing H₂O₂ only if the radiolysis occurs as water is condensing onto a surface (see Teolis *et al.* 2006). However, in dark clouds water ice is mostly formed *in-situ* at the surface of interstellar grains through surface reactions involving hydrogen and oxygen atoms. This happens prior to the formation of the presolar nebula, i.e. the cloud out of which our solar system was formed, and it is possible that the comet-forming zone of the Sun's protoplanetary disk inherited much of its water ice from the interstellar phase (Visser *et al.* 2009, Cleaves *et al.* 2014).

4. Origin of cometary O₂

4.1. Dark cloud origin?

Impact of physical and chemical parameters. We first investigated whether the O₂ observed in 67P/C-G has a dark cloud origin. For this purpose, we used the Taquet astrochemical model presented in section 2. We carried out a first parameter study, in which several surface and chemical parameters are varied, in order to reproduce the low abundances of the chemically related species O₃, HO₂, and H₂O₂ with respect to O₂ seen in comet 67P/C-G. The low abundance of O₃ and HO₂ relative to O₂ ($\leq 2 \times 10^{-3}$) can be explained when a small activation barrier of ~ 300 K is introduced for the reactions O + O₂ and H + O₂, in agreement with the Monte-Carlo modelling of laboratory experiments by Lamberts *et al.* (2013). However, the abundance of H₂O₂ is still overproduced by one order of magnitude, suggesting that other chemical processes might be at work.

A second parameter-space study was then conducted to determine the range of physical conditions over which O₂ ice and gas (and those for chemically-related species, O₃, HO₂, and H₂O₂) reach abundances (relative to water ice) similar to that seen in 67P/C-G. We ran a model grid in which four or five values for the total density of H nuclei, n_{H} , the gas and dust temperature, T (assumed to be equal), the cosmic ray ionisation rate, ζ , and the visual extinction, A_{V} are considered, following the methodology described in Taquet *et al.* (2012), resulting in 500 models in total. We explored the distribution of abundances of solid O₂, and the chemically related species, O₃, HO₂, and H₂O₂, relative to water ice, when the time reaches the free-fall time, t_{FF} . The results show that the formation and survival of solid O₂, and other reactive species, in interstellar ices, is strongly dependent upon the assumed physical conditions with abundance distributions ranging over several orders of magnitude. High O₂ abundances ($\geq 4\%$ relative to water ice) are obtained only for the models with high densities ($n_{\text{H}} \gtrsim 10^5 \text{ cm}^{-3}$). Higher gas densities result in a lower gas-phase H/O ratio, thereby increasing the rate of the association reaction between O atoms to form O₂ ice, and correspondingly decreasing the rate of the competing hydrogenation reactions, O + H and O₂ + H, which destroy O₂ ice once formed. An intermediate temperature of 20 K is also favoured because it enhances the mobility of oxygen atoms on the grain surfaces whilst at the same time allowing efficient sublimation of atomic H. This additionally enhances the rate of oxygen recombination forming O₂, with respect to the competing hydrogenation reactions. Moreover, because the density of gas-phase H atoms increases linearly with the cosmic-ray ionisation rate, ζ , a low value of ζ also tends to favour the survival of O₂ ice. On the other hand, the visual extinction does not have a strong impact on the abundance of solid O₂.

The ρ Oph A case. The parameter study presented above therefore suggests that the physical conditions of ρ Oph A, presenting a high density ($n_{\text{H}} \sim 10^6 \text{ cm}^{-3}$), and a relatively warm temperature for a starless core ($T_{\text{kin}} = 24 - 30 \text{ K}$ and $T_{\text{dust}} \sim 20 \text{ K}$; Bergman *et al.* 2011a) are consistent with those which facilitate the formation and survival of O_2 ice. This confirms that these properties offer optimal conditions for an efficient production of solid O_2 since ρ Oph A is the only interstellar source so far where gas-phase O_2 , HO_2 , and H_2O_2 have been detected. Figure 1 shows the chemical composition of the ice and gas obtained for the model using the physical conditions of ρ Oph A and that best reproduce the observations in comet 67P/C-G. The fractional composition in each ice monolayer is plotted as function of monolayer number, i.e. the ice thickness that grows with time. O_2 ice is mostly present in the innermost layers of the ice mantle and decreases in relative abundance towards the ice surface, reflecting the initial low ratio of H/O in the gas phase obtained at high densities, but tends to be well mixed with H_2O ice. CO_2 is also highly abundant because the higher temperature (21 K) enhances the mobility of heavier species, such as O or CO.

O_2 , O_3 , HO_2 , and H_2O_2 are mostly, and potentially only, produced via surface chemistry; hence their gas-phase abundances depend on their formation efficiency in interstellar ices and on the probability of desorption upon formation through chemical desorption (thought to be the dominant desorption mechanism for these species in dark cloud conditions). The chemical desorption probabilities are highly uncertain and mainly depend on the ice substrate and the considered reaction. Figure 1 shows the temporal evolution of the gas phase abundances of O_2 , O_3 , HO_2 , and H_2O_2 when the theoretical values by Minissale *et al.* (2016) relative to a bare grain substrate, and varying between 0 and 70%, are used. This model is almost able to simultaneously reproduce the gaseous abundances of O_2 , HO_2 , and H_2O_2 derived in ρ Oph A since the predicted O_2 abundance and the HO_2 and H_2O_2 abundances reach the observations at similar timescales (1.5×10^4 vs 2.2×10^4 yr). Using lower chemical desorption probabilities relevant to water ice substrates could improve the comparison with the observations.

Molecular nitrogen vs carbon monoxide and molecular oxygen. In contrast to O_2 , it is seen that CO and N_2 are mostly formed in the outer part of the ices and would, therefore, undergo a more efficient sublimation, either thermally or through photo-evaporation, during their transport from dark clouds to forming disks in the subsequent protostellar collapse phase. The chemical heterogeneity predicted in ices can therefore naturally explain the high correlation between O_2 and H_2O signals together with the weak correlation between CO, N_2 , and H_2O signals measured in comet 67P/C-G. However, it cannot explain the low N_2/CO abundance ratio of $\sim 0.6 \%$ observed in comet 67P/C-G since our dark cloud model predicts a N_2/CO of 50 %.

As shown by dynamical models of protoplanetary disk formation, volatile species that evaporated during their journey from dark clouds to upper disk layers can subsequently freeze-out onto ices again once they reach the colder disk midplane (see Drozdovskaya *et al.* 2014). N_2 is known to be slightly more volatile than CO with a binding energy lower by $\sim 150 \text{ K}$ for H_2O ice and by $\sim 60 \text{ K}$ for pure ices (Bisschop *et al.* 2006, Fayolle *et al.* 2016). We investigated the impact of these slightly different binding energies with a toy model on the recondensation of CO and N_2 during a cooling from 50 to 20 K that could occur during the transport of material from the upper disk layers to the disk midplane, assuming a constant density typical of a disk ($n_{\text{H}} = 10^8 \text{ cm}^{-3}$) and that all CO and N_2 are initially in the gas phase. It is found that CO does freeze out more efficiently than N_2 , inducing a low N_2/CO abundance ratio in ices down to 0.2% at 28 K before a re-increase to the initial abundance ratio at lower temperatures. A cooling of ices down to 26 - 28 K

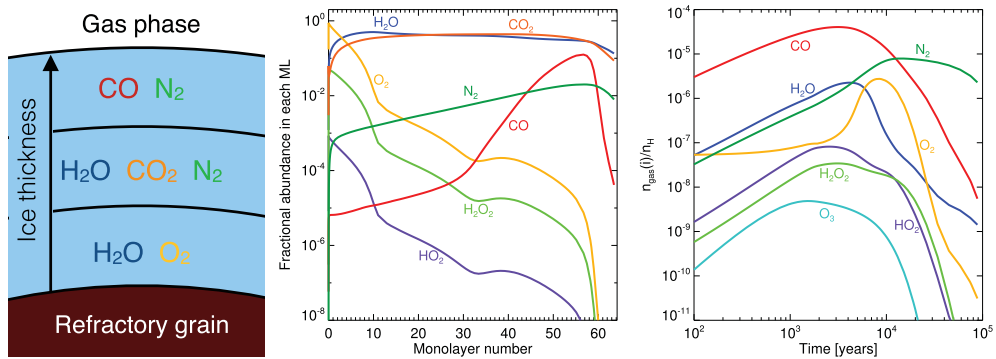


Figure 1. Left panel: Cartoon representation of the ice structure predicted in this work. Middle panel: Fractional composition of each ice monolayer as function of the monolayer number or ice thickness. Right panel: gas phase abundances as a function of time (right panel) of O_2 and its chemically related species predicted by the model using the ρ Oph A physical conditions.

near the cometary zone therefore induces a CO/H_2O abundance higher than 10% and a N_2/CO abundance lower than 0.6%, even if a high initial N_2/CO abundance is produced in the dark cloud phase. These numbers are close to those observed for 67P/C-G.

4.2. Disk formation origin?

Here, we discuss the role of chemistry during protostellar collapse and protoplanetary disk formation on the observed abundance of O_2 in 67P/C-G. To follow the chemical evolution from prestellar cores to forming disks, fluid parcels from the envelope to the disk are traced with the physical model initially developed by Visser *et al.* (2009). The Furuya astrochemical model is used to follow the gas-ice chemical evolution calculated along each individual trajectory. The physical model used here is an axisymmetric semi-analytical two-dimensional model that describes the temporal evolution of the density and velocity fields following inside-out collapse and the formation of an accretion disk described by the α -viscosity prescription (for details, see Harsono *et al.* 2013 and references therein). The model follows the physical evolution until the end of the main accretion phase when the gas accretion from the envelope onto the star-disk system is almost complete. A molecular cloud formation model is run to determine the composition of the gas and ice in the parent molecular cloud (Furuya *et al.* 2015). The chemistry is then evolved for an additional 3×10^5 yr under prestellar core conditions to compute the abundances at the onset of collapse. At the onset of collapse, models have a negligible O_2 ice abundance.

Figure 2 shows the spatial distributions of fluid parcels at the final time of the simulation in models in the so-called spread-dominated case (initial core rotation rate $\Omega = 10^{-13}$ s $^{-1}$). It is found that (i) some gaseous O_2 can form (up to $\sim 10^{-6}$) depending on the trajectory paths (left panels), and (ii) O_2 ice trapped within H_2O ice does not efficiently form en route into the disk (middle panels). Given that most elemental oxygen is in ices (H_2O and CO) at the onset of collapse, gaseous O_2 forms through photodissociation/desorption of H_2O ice by stellar UV photons in the warm (>20 K) protostellar envelope, followed by subsequent gas-phase reactions. The majority of parcels in each disk have a low final O_2/H_2O ice ratio, $\ll 10^{-2}$. However, the upper layers of the disk do have several parcels with a O_2/H_2O ice ratio higher than 10^{-2} . Analysis of the ice composition shows that the O_2 ice is associated with CO_2 ice rather than with H_2O . Upon water ice photodissociation, the warm temperatures encountered through the protostellar envelope mean that CO_2 ice (re)formation is more favorable than that for H_2O ice.

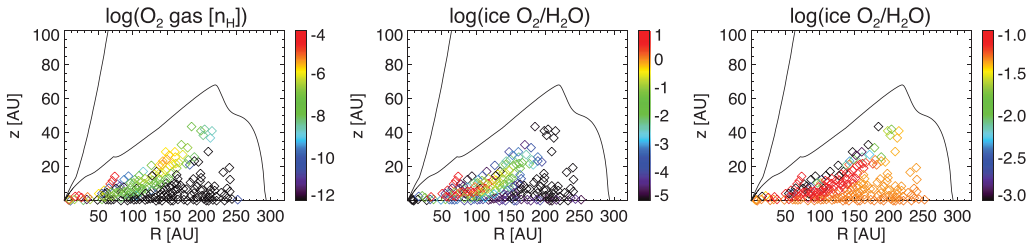


Figure 2. Spatial distributions of fluid parcels at the final time of the streak-dominated disk formation simulation ($\Omega = 10^{-13} \text{ s}^{-1}$). The left panel shows the gaseous O_2 abundance with respect to hydrogen nuclei, the middle panel shows the abundance ratio between O_2 ice and H_2O ice, the right panel also shows the abundance ratio between O_2 ice and H_2O ice, but for the model where the initial ratio is artificially set to 5%. The solid lines represent the outflow cavity wall and the disk surface.

We also considered a case where the simulations begin with a similar fraction of O_2 ice to what is observed in comet 67P/C-G (5% relative to water ice). The $\text{O}_2/\text{H}_2\text{O}$ ratio throughout both disks is largely preserved. Hence, O_2 which has a prestellar or molecular cloud origin, is able to survive the chemical processing en route into the comet-forming regions of protoplanetary disks. However, only little O_2 is formed during disk formation.

4.3. Luminosity outburst origin?

Observational and theoretical studies suggest that the luminosity evolution of low-mass stars is highly variable, with frequent and strong eruptive bursts, followed by long periods of relative quiescence (e.g. Hartmann & Kenyon 1985, Vorobyov *et al.* 2015). Such luminosity outbursts could have a strong impact on the morphology and the chemical composition of ices near the protoplanetary disk midplane. If the luminosity outburst is sufficiently strong, warm gas-phase formation of molecular oxygen could be triggered by the evaporation of water ice, if the peak temperature during the outburst is higher than $\sim 100 \text{ K}$. We explored the impact of a series of outbursts events in disks on the formation and recondensation of O_2 , increasing the temperature from 20 to 100 K, every 10^4 yr for a total timescale of 10^5 yr . The Taquet astrochemical model described previously was used. Initial ice abundances are the median values derived by Öberg *et al.* (2011) from interstellar ice observations towards low-mass protostars. Thus it is assumed that the ice mantles are initially poor in O_2 . The pre-outburst and post-outburst temperature is set to 20 K. Protoplanetary disk models suggest that the corresponding midplane density at this point is $\sim 10^8 \text{ cm}^{-3}$ (e.g. Walsh *et al.* 2014).

We varied several parameters that are thought to impact the gas phase formation of O_2 during the outburst and the efficiency of recondensation during the cooling, such as the grain size, the cosmic ray ionisation rate, the cooling timescale after the outburst or the peak temperature. It is found that the maximum amount of O_2 formed during luminosity outbursts and then trapped within the ice mantle during the cooling does depend on the explored parameters but never exceeds $\sim 0.1\%$ w.r.t. H_2O ice. This suggests that luminosity outbursts are too short to significantly produce O_2 with quantities similar to those observed in comet 67P/C-G. Assuming an initial O_2 abundance of 5% relative to water ice results in efficient trapping of O_2 within the water-ice mantle due to the fast cooling after the outburst. However, in that case also other volatile species, such as CO and N_2 , become trapped, which is in contradiction with observations towards 67P/C-G.

5. Conclusions

The models presented here favour the scenario that molecular oxygen in 67P/C-G has a primordial origin (i.e., formed in the parent molecular cloud) and has survived transport through the protostellar envelope and into the comet-forming regions of protoplanetary disks. The “primordial” origin of O₂ is in good agreement with the conclusions of Mousis *et al.* (2016). Mousis *et al.* (2016) invoked radiolysis to efficiently convert water ice to O₂. However, we find here that the entrapment and strong association with water ice combined with low abundance of species like H₂O₂, HO₂, or O₃ can be explained by an efficient O₂ formation at the surface of interstellar ices through oxygen atom recombination in relatively warmer (~ 20 K) and denser ($n_{\text{H}} \gtrsim 10^5 \text{ cm}^{-3}$) conditions than usually expected in dark clouds. The weak correlation of CO and N₂ with water seen in 67P/C-G is explained by a later formation and freeze-out of these species in dark clouds with respect to O₂ and water. This picture would therefore be consistent with the physical and chemical properties of our Solar System, such as the presence of short-lived radio isotopes in meteorites or the orbits of Solar System planets, which suggests that our Solar System was born in a dense cluster of stars (see Adams 2010).

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Discussion