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Towards a unique formation and trapping scenario of O_2 and S_2 in comets

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Abstract

Following the observations by the ROSINA-DFMS instrument on board of Rosetta spacecraft, the processes of formation of O_2 and S_2 in comets are actually quite disputed and a consistent interpretation of all the data is still to be found. Computational chemistry models based on first principle periodic density functional theory (DFT) are well adapted to the description of compact ice and are shown here to be capable to provide the quantitative data to support the following scenario for O_2 and S_2 origin in 67P. In this scenario, assuming that both, O_2 and S_2, should have similar ways of formation, storage and release, we propose that these dimers were formed inside the icy grains precursors of comets in low-density environments by irradiation, photolysis and/or radiolysis, which creates simultaneously voids in the compact ices, voids within which the molecules produced can be trapped efficiently enough to be liberated only simultaneously with the water ices.

1. Observational background

The search for O_2 in space has been carried on for years to no avail, even if now some old observations are re-considered as positive; on the contrary, S_2 has been observed for decades in comets. Nevertheless, both molecules suddenly arose a new interest following their observation in comet 67P/Churyumov-Gerasimenko (67P/C-G) [1] [3]. The ROSINA-DFMS instrument on board of the Rosetta spacecraft detected molecular oxygen in the coma with an unexpected range of abundances (1–10% with respect to H_2O) and a surprising correlation with H_2O. Concerning S_2, the abundance observed is much lower though significant (~10^{-5} with respect to H_2O) but shows no correlation with H_2O [2].

2. One formation scenario

We propose that both molecules, O_2 and S_2, are formed in the icy grain precursors of comets by irradiation (photolysis and/or radiolysis) respectively of the H_2O ices themselves, or of the S-bearing molecules embedded in the H_2O ices. The cosmic ray flux simultaneously creates voids in the matrix within which the so produced molecules can accumulate.
For both molecules, such a formation inside the grains must occur in low-density environments such as the ISM or the upper layers of the protosolar nebula, where the local temperature is extremely low. In the first case, comets would have agglomerated from icy grains that remained pristine when entering the nebula. In the second case, comets would have agglomerated from icy grains condensed in the protosolar nebula and that would have been efficiently irradiated during their turbulent transport toward the upper layers of the disk.

2.1 The case of O_2

In this scenario, the irradiation is assumed to break the H_2O molecules along their tracks, inducing a chemistry of highly reactive radicals as H, O, OH, leading in particular to the formation of O_2. The voids created simultaneously in the compact ices home the molecules produced and keep them trapped efficiently enough to get them liberated only when the water ices sublimate, even if a moderate heating eventually occurs, allowing an amorphous-to-crystalline phase transition.

Indeed, we have studied the stability of the O_2 molecules in different types of cavities (Table 1), and got the following results: i) no stabilization can be found neither for the inclusion of O_2 in the hexagonal ice lattice, nor for the replacement of a H_2O by O_2, ii) by contrast, the irradiation of the ice by cosmic rays generates cavities in which molecular oxygen is perfectly stable under the form of O_2 or even of dimers of O_2, a possibility which allows to interpret the variations of the proportion O_2/H_2O observed [4].

Table 1: Stability (eV) of O_2 in voids within the ice (n: number of molecules removed to create the void)

Environment	H_2O ices
Inclusion (n=1)	0.00
Inclusion (n=2)	0.23
Inclusion (n=4)	0.25
Inclusion (fine track)	0.24
Inclusion (large track)	0.30

2.2 The case of S_2

It is well known chemically that S-bearing molecules embedded in H_2O ices turn easily to SH_2 under irradiation effects, making possible the creation of sort of clumps within the H_2O lattice; knowing that, under more irradiation, the SH_2 molecules convert themselves into S_2 and even larger oligomers, we considered again the possibility that these molecules can accumulate in the voids created simultaneously in the icy matrix.

We have investigated the stability of the S_2 molecules in such cavities, assuming that the surrounding ice could be made of H_2S or H_2O (Table 2). We show that the stabilization energy of S_2 molecules in such voids is close to that of the H_2O ice binding energy, implying that they can only leave the icy matrix when this latter sublimates.

Table 2: Stability (eV) of S_2 in voids within the ice (n: number of molecules removed to create the void)

Environment	H_2O ices	H_2S ices
Inclusion (n=1)	Non stable	0.30
Inclusion (n=2)	0.30	0.40
Inclusion (n=4)	0.50	0.40
Inclusion (fine track)	0.51	0.41
Inclusion (large track)	0.53	0.50

However, as S_2 can be trapped in H_2O as well as in SH_2 environments, no correlation has to be found with H_2O emission [5].

3. Summary and Conclusions

Both molecules O_2 and S_2 detected in the coma of 67P/C-G might have been formed inside the icy grains precursors of comets in low-density environments as a consequence of the cosmic rays irradiation. Using computational chemistry models based on first principle periodic density functional theory (DFT), we have evaluated the stability of these species in the irregular cavities of the irradiated compact ices, revealing a strong stabilization, efficient enough to keep them trapped until the ices sublimate.

The high abundance observed for O_2 can be explained by the quasi-unlimited raw material available, H_2O. It should be stressed that the formation of one O_2/S_2 requires at least the destruction of two H_2O /SH_2 whatever the chemical reactions involved. Consequently, O_2 formed and trapped only in an H_2O environment should be correlated strongly to the H_2O emission, contrary to S_2 possibly formed and trapped in different matrices.

Specific calculations on the chemistry of formation of the two species inside the icy bulk are actually in progress.

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