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Memorie della

My chemistry with Francesco

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Abstract. Through all his career, Francesco maintained a keen interest in primordial star formation and the chemistry of the early Universe. It was therefore quite natural for me, his former student and his officemate for more than 12 years, to be also involved in these studies. In this contribution I summarize the chemistry that Francesco and I developed, pointing out the main findings and false steps of our lifelong collaboration.

Key words. Early Universe – Molecular processes – Atomic Processes

1. Introduction

In the summer of 1987, Ralph Pudritz and Michel Fich organized a NATO School on "Galactic and Extragalactic Star Formation" in Whistler, a resort town in beautiful British Columbia, where Francesco was invited to give a review lecture on "Primordial Star Formation". Among the participants to the School were three PhD student of the University of Florence (Riccardo Cesaroni, Paolo Lenzuni and myself), and the somewhat more mature Director of the Arcetri Observatory (Franco Pacini). For the three of us, the youngest members of this scientific expedition, the 1987 NATO School was the first experience of an international astronomical conference, and, in my case, my first exciting contact with the great American continent. A picture taken during the School (Fig. 1) shows a relaxing moment during one of our excursions, when Francesco and Franco Pacini engaged in a resistance contest in the freezing-cold waters of the Garibaldi Lake (for the records, Francesco lost). Francesco's lecture, published one year later (Palla 1988), stimulated my interest in the chemistry of the early Universe, and our discussions during long walks in the Canadian woods marked the beginning of a lifelong collaboration with him on this subject.

It is instructive to look in retrospect at the topics that Francesco addressed in his 1987 lecture, to assess the progress (or the lack of it) and the expected (or unexpected) developments that have occurred in this field in the intervening 30 years. Francesco's lecture covered four broad subjects:

(1) the search for zero-metal stars,
(2) the chemistry of the early Universe,
(3) the evolution of collapsing gas clouds, and
(4) the formation of primordial stars.

These topics are still in the forefront of current research, as also witnessed by these Proceedings. In his lecture, Francesco gave also a summary of his own work done in collaboration with Ed Salpeter and Steve Stahler that had been published only a few years before: the famous Palla-Salpeter-Stahler (and permutations) "trilogy" of 1983–1986 (Palla et al. 1983; Stahler et al. 1986a,b)

Our collaboration on primordial chemistry developed from these premises. The first paper of the trilogy (which is Francesco's most cited paper) pointed out the importance of 3-body reactions, $3H \rightarrow H_2 + H$ and $2H + H_2 \rightarrow H_2 + H_2$ for the gas-phase formation of molecular hydrogen. The conversion of H into H_2 was followed with the help of a very simple model for the collapse of a zero-metal cloud. Francesco was aware of the limitations of the collapse model and the chemical network adopted, and wanted to improve both. Even though his main interest was on the former aspect (collapse and star formation), we resolved to work first on the latter (the chemistry), and continued to do so until 2013. The motivation for proceeding in this order was the poor state of primordial chemistry at the time, with many reaction channels poorly identified, reactions rates badly guessed and often largely discrepant from author to author, and the relevant data scattered in publications not easily accessible (it was before the ADS). Especially annoying was the uncertainty on the H_2 cooling rate for collisions with H atoms. In the 1980's, two independent calculation of this fundamental ingredient for any recipe of primordial star formation were available: one by Lepp & Shull (1983), and one by Hollenbach & McKee (1979, revised in 1989), based on independent sets of collisional rate coefficients. The problem was that the two cooling rates in the low-density regime differed by as much as one order of magnitude or more below $T \approx 100$ K, a temperature range relevant for collapse calculations. As a result, the estimate of the minimum mass needed to collapse at redshift $z \approx 30$–40 was uncertain by a factor of ~ 30 (see e.g. Fig. 7 of Palla 1999). Clearly, before attacking our planned collapse calculation, a systematic and critical reanalysis of the microphysics was in order. The collapse calculation we originally planned was eventually done, but not by us. The work by Kazuyuki Omukai and coworkers is in my opinion the ideal fulfilment of our program (Omukai & Nishi 1998, Omukai 2000). Later on, Francesco would "exploit" K. Omukai's capabilities to further develop his trilogy papers: first, to explore the formation of massive stars by the enhanced accretion rate expected in primordial conditions (Omukai & Palla 2001); and, second, to extend his 1986 calculation of the mass-radius relation for protostars to the case of a zero-metallicity cloud (Omukai & Palla 2003).

Fig. 1. Francesco Palla and Franco Pacini swim in the Garibaldi Lake, British Columbia (July 1987).

Turning back to our chemistry, our critical selection and analysis of gas-phase reaction rates for a mixture of H, He, D, Li and their products was eventually completed and published in 1998, together with our "new and improved" cooling rates for the main molecular species (Galli & Palla 1998). Our recommended reaction and cooling rates were widely adopted by researchers in the field (Galli & Palla 1998 is my most cited paper), showing that the humble work of reordering and systematizing can be useful too. Ten years later, the H-H_2 cooling rate by Galli & Palla (1998) was superseded by a newer calculation by Glover & Abel (2008), based on updated collisional rate coefficients. The last word on the subject is represented in my opinion by the extensive set of theoretical calculations performed by François Lique and coworkers (Lique et al. 2012; Lique 2015) of H-H_2 collisional cross sections and rate coefficients down to temperatures of 10 K, whose impact on the H-H_2 cooling rate still needs to be fully assessed.

In 2013 Francesco and I were invited to write an Annual Reviews paper on primordial chemistry. For us this was a good opportunity to summarize the latest developments in a historical context (Galli & Palla 2013). We realized that in the intervening years many of the uncertainties that affected the results of Galli & Palla (1998) had been largely overcome: first of all, cosmology had entered the "precision era", and the uncertainty on the chemistry of the Dark Ages was no longer dominated by uncertainties in the values of the cosmological parameters (all accurately determined by Boomerang, Planck and WMAP), but by residual uncertainties in the chemical reaction rates. These, fortunately, were found to be very small at least for the key reactions, with the possible exception of the 3-body reactions mentioned earlier, and others of minor relevance. The 2013 review was the last paper I had the privilege and the pleasure of writing sitting side-by-side with Francesco. It was, as always, an enjoyable personal experience: Francesco was dead serious about science, careful and rigorous in his work, but at the same time light-hearted, playful and full of irony with his coworkers. Francesco and I were also curious about the possible observational signatures left by primordial molecules in the form of both spatial fluctuations and spectral distortions in the cosmic microwave background (CMB). This idea was first advanced by Viktor Dubrovich in the 1970's (Dubrovich 1977), endorsed by Zel'dovich (1978), and later developed in depth by Prof. Francesco Melchiorri and his group at the University La Sapienza in Rome, where Francesco had studied (Maoli et al. 1994, 1996). The attractive feature of this proposal was that a hypothetical absorbing layer of molecules extending over a significant range of redshifts could erase or attenuate primary anisotropies produced at higher redshift, reconciling cosmological models of structure formation with the small magnitude and large angular scale of the spatial anisotropies known at the time. The attention concentrated on the LiH molecule, due to its high dipole moment, and its (expected) efficient formation by radiative association. Unfortunately, the latter process was found to occur at a very slow rate (Dalgarno et al. 1996; Gianturco & Gori Giorgi 1997), too slow for LiH to play any significant role in the early Universe. It was however exciting for Francesco and myself to get involved in the laboratory frequency measurements of 14 rotational transitions of LiH in the fundamental and in the first two excited vibrational states (Bellini et al. 1994), and collaborate with Prof. Francesco Gianturco of the University of Rome and his student Stefano Bovino on accurate determinations of reaction rates relevant for the gas-phase chemistry of Li and He (Bovino et al. 2011a,b; 2012). Then, in collaboration with a young brilliant post-doc, Dominik Schleicher, who visited the Arcetri Observatory during 2008, we computed the distortions imprinted in the CMB by the chemistry taking place during the Dark Ages (Schleicher et al. 2008, 2009). The changes in the CMB intensity and power spectrum were found to be too small to be detected by Planck, but within reach of planned future CMB satellite like PIXIES and PRISM. The most promising species from this point of view were identified in H^- (as also suggested by Black 2006) and HeH^+. A few years later Francesco and I met another bright freshly graduated young researcher, Carla Maria Coppola of the University of Bari, who patiently and skilfully educated both of us through the intricacies of state-resolved chemistry, in particular of H_2 and H_2^+, and the subtle effects of non-thermal (recombination) photons (Coppola et al. 2011, 2012, 2013, 2016, 2017). Our work also benefited from many discussions with Raffaella Schneider, first met by Francesco and myself at a cosmology meeting in Frascati in 1996, where a just graduated Raffaella delivered her talk with a mix of intelligence and grace that has remained unchanged over the years.

My chemistry with Francesco was not limited to primordial molecules: we were both very curious about primordial isotopes as well, in particular D and ^{3}He (Galli et al. 1995). The latter isotope was especially intriguing, and a lot of effort was devoted to understand why, if ^{3}He is produced by low-mass stars as predicted by stellar nucleosynthesis models, its present-day abundance measured in HII regions and the local ISM, as well as in gas-rich meteorites, is about one order of magnitude lower than it should be. It was an interesting problem, since this discrepancy, the so-called "^{3}He problem" hampered the use of this isotope as a cosmic baryometer along with D, ^{4}He and ^{7}Li (the latter being problematic as well, see Paolo Molaro's contribution in these Proceedings). We found an elegant nuclear physics solution to this problem (Galli et al. 1994), but the ugly truth was eventually discovered by Charbonnel (1995) and Hogan (1995) in the form of a non-standard mixing mechanism acting in low-mass stars during the red-giant branch evolution or later, leading to a substantial (or complete) destruction of all their freshly produced ^{3}He. However, we were in some sense vindicated by the observational evidence that at least *some* stars do not appear to suffer extra-mixing during all their lives (Galli et al. 1997).

This was my chemistry with Francesco: curiosity-driven research and the pure pleasure of sharing knowledge with others. My chemistry partner has truly enriched my life.

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