HYDROGEN/DEUTERIUM EXCHANGES IN INTERSTELLAR/COMETARY ICE ANALOGS

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Despite the low cosmic abundance of deuterium (D/H ~ 10^{-5}), high degrees of deuterium enrichment in molecules are observed in star-forming regions with enhancements that can reach 13 orders of magnitude for multi-deuterated species [1]. High D/H ratios are also observed in planets and small bodies of the solar system. Quantitative modelling of the D/H ratios remains however hampered by the lack of appropriate chemical kinetics data. In particular, the detailed mechanisms responsible for the observed enrichment disparities between functional groups are currently poorly known. For example, there is significantly more CH_2DOH than CH_3OD ($[CH_2DOH]/[CH_3OD]>10$) in low-mass protostars [2]. Various hypotheses have been suggested to explain this anomaly, but none is fully convincing. In this work, we test a new hypothesis experimentally: the spontaneous exchange between hydrogen and deuterium atoms in H_2O:XD ice mixtures, where XD is either CD_3OD (methanol) or CD_3ND_2 (methylamine).
To this aim, thin films of intimate H_2O:XD ice mixtures, condensed at low temperature ($\leq$ 110K), have been monitored by Fourier transform infrared (FTIR) spectroscopy up to the complete evaporation of XD molecules. Rapid hydrogen/deuterium (H/D) exchange has been observed, at 120K and above, through the growth of the ν_{OD} stretching mode of HDO at 2425 cm^{-1}. It has been also shown that H/D exchange occurs (i) on the hydroxyl and amino functional groups of XD molecules, i.e. through hydrogen bonds, and (ii) before the completion of crystallization. The present results suggest therefore that the much lower abundance of CH_3OD compared to CH_2DOH in low-mass protostars could simply reflect H/D exchanges in water ice either prior to or during the grain mantle sublimation [3]. This hypothesis will be further discussed in view of new millimeter observations of singly deuterated methanol towards high- and intermediate-mass protostars. Finally, new experimental data including the kinetics of H/D exchanges will be presented and the physical processes expected to promote or limit these exchanges in space will be emphasized.

References

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