Kinetics of hydrogen/deuterium exchanges in cometary ices

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The D/H composition of volatile molecules composing cometary ices brings key constraints on the origin of comets, on the extent of their presolar heritage, as well as on the origin of atmospheres and hydrospheres of terrestrial planets. Nevertheless, the D/H composition may have been modified to various extents in the nucleus when a comet approaches the sun and experiences deep physical and chemical modifications in its subsurface. In this talk, we question the evolution of the D/H ratio of organic species by proton exchanges with water ice. We experimentally studied the kinetics of D/H exchanges on the ice mixtures $H_2O:CD_3OD$, $H_2O:CD_3ND_2$ and $D_2O:HCN$. Our results show that fast exchanges occur on the -OH and -NH_2 chemical groups, which are processed through hydrogen bonds exchanges with water and by the molecular mobility triggered by structural changes, such as glass transition or crystallization. D/H exchanges kinetic is best described by a second-order kinetic law with activation energies of 4300 ± 900 K and 3300 ± 100 K for $H_2O:CD_3OD$ and $H_2O:CD_3ND_2$ ice mixtures, respectively. The corresponding pre-exponential factors $\ln(A(s^{-1}))$ are 25±7 and 20±1, respectively. No exchange was observed in the case of HCN trapped in D_2O ice. These results strongly suggest that upon thermal heating 1) -OH and -NH_2 chemical groups of any organic molecules loose their primordial D/H composition and equilibrate with water ice, 2) HCN does not experience proton transfer and keeps a primordial D/H composition and 3) C-H chemical groups are not isotopically modified.