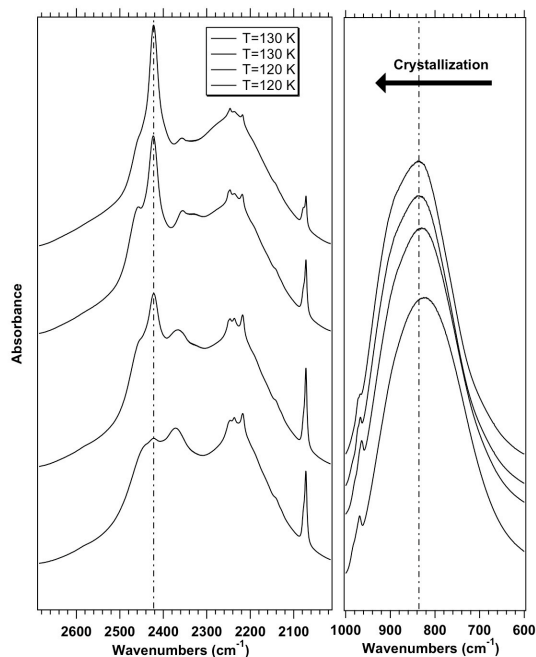


**SPONTANEOUS D-H EXCHANGE BETWEEN WATER ICE AND COMPLEX ORGANIC MOLECULES (COMS) IN PROTOSTELLAR ENVIRONMENTS.** A. Ratajczak<sup>1,2</sup>, E. Quirico<sup>2</sup>, A. Faure<sup>1</sup>, B. Schmitt<sup>2</sup>, and C. Ceccarelli<sup>1</sup>. <sup>1</sup>Laboratoire d'Astrophysique Observatoire de Grenoble CNRS-Université Joseph Fourier 38041 Grenoble Cedex 9 France ; <sup>2</sup>Laboratoire de Planétologie de Grenoble CNRS-Université Joseph Fourier 38041 Grenoble Cedex 9 France

Multiply deuterated isotopologues of methanol have been detected in gas-phase in the protostar IRAS16293-2422 [1]. In this source, there is significantly more CH<sub>2</sub>DOH than CH<sub>3</sub>OD. The origin of this selective deuteration is not understood. Gas-phase chemistry modeling does not account for this multiplydeuteration [2], therefore cold atoms reactions onto the surface of the grains have been favoured thanks to experimental simulations [3,4]. In this work, we test experimentally the hypothesis of spontaneous exchange between hydrogen and deuterium atoms in interstellar ice analogs composed of CD<sub>3</sub>OD and H<sub>2</sub>O. Thin films of intimate H<sub>2</sub>O:CD<sub>3</sub>OD ice mixtures, condensed at low temperature (<110 K), are monitored by Fourier transform infrared (FTIR) spectroscopy up to the complete evaporation of CD<sub>3</sub>OD (~170 K). Rapid hydrogen/deuterium (H/D) exchange is observed, at 120 K and above, through the growth of the  $\nu_{OD}$  stretching mode of HDO at ~2425 cm<sup>-1</sup>. It is also shown that H/D exchange occurs i) on the hydroxyl functional group of methanol, i.e through hydrogen bonds, and ii) before the completion of crystallization. The present results suggest that the much lower abundance of CH<sub>3</sub>OD compared to CH<sub>2</sub>DOH in IRAS16293-2422 could reflect H/D exchanges in water ice prior or during the grain mantle evaporation. This solid-state depletion mechanism, so far neglected in the astronomical literature, is expected to affect other deuterated molecules with hydrogen bonds, i.e. containing -OH, -NH- or -NH<sub>2</sub> functional groups [5]. This mechanism is expected to occur at any step of stellar evolution, as long as icy grains are expected to experience sublimation-condensation cycles. It is also suspected to occur in the solar nebula, and should be taken into account for interpreting the D/H ratio in organic compounds and water molecules, in comets and meteorites.

**References:** [1] Parise, B., Castets, A., Herbst, E., et al. 2004, A&A, 416, 159 ; [2] Garrod, R., Park, I. H., Caselli, P., & E. H. 2006, Faraday Discuss., 133, 51 ; [3] Nagaoka, A., Watanabe, N., & Kouchi, A. 2005, ApJ, 624, L29 ; [4] Watanabe, N. & Kouchi, A. 2002, ApJ, 571, L173 ; [5] Ratajczak et al. 2009, A&A, 96, L21



**Figure 1:** Left: the D<sub>H</sub> exchange is monitored by the increase of the  $\nu_{OD}$  band of HOD (2425 cm<sup>-1</sup>); Right: the exchange begins before the completion of crystallisation, pointed out by the libration band of water ice at ~840 cm<sup>-1</sup>.