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LETTER TO THE EDITOR

Hydrogen/deuterium exchange in interstellar ice analogs

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ABSTRACT

Context. For several reasons, methanol is believed to be formed on grain surfaces and, in warm environments, released in the gas phase. In the past, multiply deuterated isotopologues of methanol have been detected in gas phase around several low-mass protostars. In all these sources, there is significantly more CH_2DOH than CH_3OD. Various hypotheses have been suggested to explain this anomaly, but none is fully convincing.

Aims. In this work, we test a new hypothesis experimentally: the spontaneous exchange between hydrogen and deuterium atoms in water ice as responsible for the deficiency of CH_3OD with respect to CH_2DOH.

Methods. We follow the temperature dependence of the composition of interstellar ice analogs initially composed of CD_3OD and H_2O. To this aim, thin films of intimate H_2O:CD_3OD ice mixtures, condensed at low temperature (<110 K), are monitored by Fourier transform infrared (FTIR) spectroscopy up to the complete evaporation of CD_3OD (∼170 K).

Results. Rapid hydrogen/deuterium (H/D) exchange is observed, at 120 K and above, through the growth of the ν_{OD} stretching mode of HDO at ∼2425 cm^{-1}. 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.

Conclusions. The present results suggest that the much lower abundance of CH_3OD compared to CH_2DOH in low-mass protostars could reflect H/D exchanges in water ice either prior to or definitely during the grain mantle sublimation. This solid-state depletion mechanism, so far neglected in the astronomical literature, might affect other deuterated molecules with hydrogen bonds.

Key words. molecular data – molecular processes – ISM: molecules

1. Introduction

A variety of interstellar molecules are highly enriched in deuterium. This well-known phenomenon, first discovered by Jefferts et al. (1973), was soon interpreted (Wilson et al. 1973) as occurring at a low temperature because of the differences in zero-point energies between deuterated and nondeuterated species. Recent observations towards regions of high density and heavy CO depletion, such as prestellar cores, have revealed that the gas-phase abundances of singly deuterated molecules are typically four orders of magnitude higher than the cosmic atomic D/H ratio of 1.5×10^{-5} (Linsky 2003). Even more spectacular, doubly and triply deuterated molecules have been observed with D/H ratios reaching ∼30% for D_2CO (Ceccarelli et al. 1998; Loinard et al. 2002) and ∼3% for CD_3OH (Parise et al. 2004). It should be noted that this extreme deuteration has been observed only in low-mass (solar-type) prestellar cores and protostars (Ceccarelli et al. 2007). A theoretical point of view has shown (Roberts et al. 2003) that the multiply deuterated isotopologues of H_3^+ efficiently transfer deuterons to other neutral molecules in very cold (≤20 K) gas depleted of its CO (because frozen onto the grain mantles). At the same time, the dissociative recombination of the deuterated ions leads to significant enhancement of the atomic D/H ratio (>0.1). As a consequence, molecules formed in the gas phase (e.g., Roueff et al. 2007) or onto the grain surfaces by atom addition reactions (e.g., Tielens 1983) would present large enhancements of the D- over H-bearing molecules with respect to the cosmic D/H abundance ratio.

In the case of methanol, in particular, recent experimental works have demonstrated that a purely gas-phase synthesis is unlikely to reproduce the observed abundances (see Garrod et al. 2006, and references therein), while the hypothesis of methanol formation on cold grain surfaces by successive hydrogenation of CO has apparently been confirmed (Nagaoka et al. 2005). Moreover, Nagaoka et al. (2005) were able to reproduce a level of deuterium fractionation of methanol comparable to observations, including multiply deuterated isotopologues. These authors have shown, in particular, that the deuteration proceeds (in their experiment) mainly via the H-D substitution in solid methanol rather than via the successive hydrogenation and deuteration of CO. Furthermore, the non-detection of CH_3OD in their experiment was claimed to be consistent with the much lower gas-phase abundance of CH_3OD compared to CH_2DOH in low-mass class 0 protostars (Parise et al. 2004, 2006). In these sources, the [CH_2DOH]/[CH_3OD] ratio was indeed found to be unexpectedly large (e.g. 20 ± 14 in IRAS 16293-2422) compared to the value of 3 predicted by a statistical surface formation mechanism (Charnley et al. 1997). Alternatively, Osamura et al. (2004) have theoretically studied the post-evaporative gas-phase chemistry of the deuterated methanol isotopologues. They show that pairs of isotopologues with deuterium at different sites (e.g. CH_3OD and CH_2DOH) cannot be interconverted efficiently. They conclude that CH_3OD could actually be destroyed in the gas phase, through protonation reactions, on a much faster time scale than CH_2DOH.

In this Letter, we test a new hypothesis that has so far not been considered in the astronomical literature to explain the observed selective deuteration of methanol: the solid-state hydrogen/deuterium (H/D) spontaneous exchange between deuterated methanol and water. Such exchanges have been studied for a long time using various experimental approaches in water ices (see e.g., Devlin & Buch 2007, and references therein). In the present work, H/D exchanges are investigated by Fourier transform infrared (FTIR) spectroscopy of H_2O:CD_3OD ice mixtures. The experimental method is described in Sect. 2. The results are presented in Sect. 3 and discussed in Sect. 4. We conclude with Sect. 5.

2. Method

Experiments were performed at the Laboratoire de Planétologie de Grenoble. Thin films of pure ices or intimate molecular mixtures of H_2O:CD_3OD were condensed at low temperature (30–110 K) onto a KBr window, located at the bottom of the cold finger of a helium closed cycle cryostat. A co-deposition system with two gas inlets injected both gases independently in the vacuum cell and ensured the lack of isotopic exchange prior condensation onto the cold window. The CD_3OD had a purity of 99.8% and H_2O of 99.9999%. The temperature was monitored with a heating resistor located onto the window holder and a PID controller. The ultra-vacuum in the cell was typically $\sim 10^{-8}$ mbars, thanks to a turbomolecular pump. Film thickness was measured during deposition from the interference fringes of the transmitted and reflected beams of an He-Ne laser. Mid-infrared spectra (4000–400 cm^{-1}) were collected with a NICOLET800 FTIR spectrometer, equipped with a GLOBAR source and a DTGS detector. The H_2O:CD_3OD molar ratio in solid films was estimated from the ratio of the condensation rates of pure H_2O and CD_3OD, assuming similar sticking coefficients (~1 at these low temperatures). However, thin film deposition continued after stopping gas injection, because of the remaining adsorbed molecules in the gas inlets. The solid film probably exhibited a concentration gradient close to its surface exposed to vacuum, and the CD_3OD concentration was probably not estimated accurately.

3. Results

Preliminary experiments consisted in condensing stacked thin films (thickness ~μm) of pure ices of CD_3OD and H_2O. No H/D exchange was observed, regardless of the temperature, duration, and experimental conditions of deposition. In contrast, rapid H/D exchanges were observed in H_2O:CD_3OD intimate molecular mixtures, as we show below.

Two significant experiments with intimate H_2O:CD_3OD mixtures are presented in the following. In the first one, a thin film was condensed at 90 K with an H_2O deposition rate of 0.15 μm.min^{-1}, a CD_3OD deposition of 8×10^{-3} μm.min^{-1}, hence a CD_3OD concentration in H_2O ice of ~3%. In this experiment, the film was monitored by FTIR spectroscopy up to the complete CD_3OD evaporation in the range 90–170 K. Infrared spectra were found to exhibit the fundamental vibrational modes of amorphous water ice, ν_1 and ν_3 as a broad band at ~3300 cm^{-1}, ν_2 as the asymmetric broad band peaking at ~1700 cm^{-1}, and the libration band ν_L at ~830 cm^{-1} (see Table 1). It should be noted that the low CD_3OD:H_2O ratio required film thicknesses leading to saturation of the strong stretch and anti-stretch fundamental water bands. The H/D exchanges were thus traced within the spectral range 2700–2000 cm^{-1} only (see Fig. 1). In this region, the most intense spectral feature is the broad water combination vibrational mode ν_2+ν_L, onto which are superimposed several modes of the CD_3 functional group of CD_3OD and, when present, the ν_{OD} stretching mode of HDO at ~2425 cm^{-1}. Vibrational modes of CD_3OD are observed at 2250 and 2225 cm^{-1} for the antisymmetric stretching modes of the CD_3 methyl group and at 2080 cm^{-1} for the CD_3 symetric stretching mode. The band of the stretching mode ν_{OD} of CD_3OD is found to merge with the broad $\nu_2 + \nu_L$ water ice combination band. This clearly reflects the presence of numerous CD_3OD multimers interacting with each other by strong hydrogen bonding (Quirico & Schmitt 1997a,b).

Table 1. The observed vibrational frequencies (cm^{-1}) of H_2O, HOD, and CD_3OD in the condensed H_2O:CD_3OD thin films.

Vibrational mode	Band position (cm^{-1})
$\nu_1(H_2O)$	~3300
$\nu_2(H_2O)$	~1700
$\nu_3(H_2O)$	~3300
$\nu_L(H_2O)$	~830
ν_2+$\nu_L(H_2O)$	~2250
ν_{OD}(HOD)	2425
$\nu_{OD}(CD_3OD)$	~2500–2350
$\nu_{CD_3}(CD_3OD)$	2250, 2225, 2080
$\delta_{CD_3}(CD_3OD)$	1115, 1065
$\nu_{CO}(CD_3OD)$	980

The first major result of this experiment is the presence, at 120 K and above, of the ν_{OD} stretching mode of HDO at ~2425 cm^{-1} (Fig. 1). We emphasize that this band was completely absent at lower temperatures, while it was found to grow rapidly at 120 K (within a few hours). We note that it cannot be assigned to monomeric CD_3OD because it is observed prior methanol sublimation, as supported by the intensity of the methyl band at 2080 cm^{-1}.

The presence of HDO in water ice after the complete sublimation of CD_3OD (at 170 K) definitely evidences the fact that a H/D transfer occured between CD_3OD and H_2O in solid state. The second crucial result concerns the location of the H/D exchange: the intensity, position, and shape of the CD_3 functional group at 2080 cm^{-1} is unaltered throughout the whole growth of the HDO ν_{OD} band (Fig. 1). This demonstrates that proton transfer occurred on the hydroxyl group of CD_3OD, presumably through hydrogen bonding.

In the second experiment, a thin film was condensed at 110 K, and the CD_3OD concentration in H_2O ice was ~1%. Time-resolved measurements were performed over ~150 h in the temperature range 110–130 K, with a better time resolution than in the first experiment. We had specific concerns with the control of the kinetics by crystallization, which is known to enhance molecular motion and to promote hydrogen bonding. As shown in Fig. 2 the spectra look slightly different from those of the first experiment. The first reason is that different CD_3OD concentrations led to different size distributions of CD_3OD clusters, resulting in variations in the spectral distribution over the $\nu_{OD}(CD_3OD)$ region. We also suspect that an almost pure CD_3OD film deposited onto the firmly deposited mixture, because of condensation of CD_3OD adsorbed in gas inlets.

Here again, no H/D exchange was observed at temperatures lower than 120 K. At $T = 120$ K, the H/D exchange was significant after only 6 h. At that time, the ν_{OD} vibrational mode of

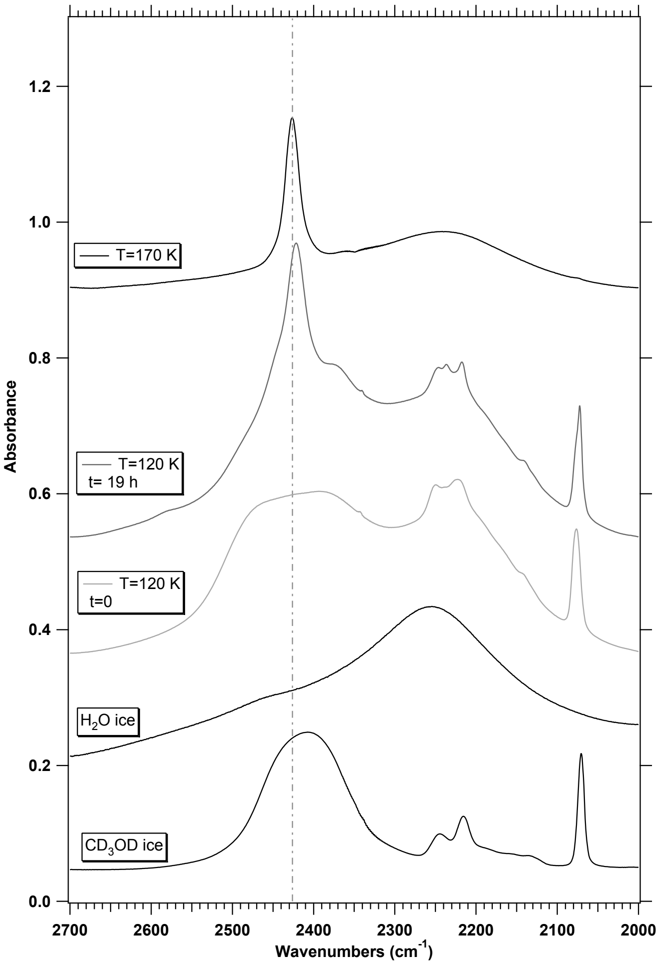

Fig. 1. First experiment (90–170 K). The isotopic exchange is monitored up to the complete evaporation of CD_3OD. The remaining crystalline (Ic) H_2O ice film is enriched in HDO. At 120 K, rapid H/D exchange occurs. The experiment shows H/D exchange located on the hydroxyl functional group. Spectra are vertically offset to ensure clarity in the figure.

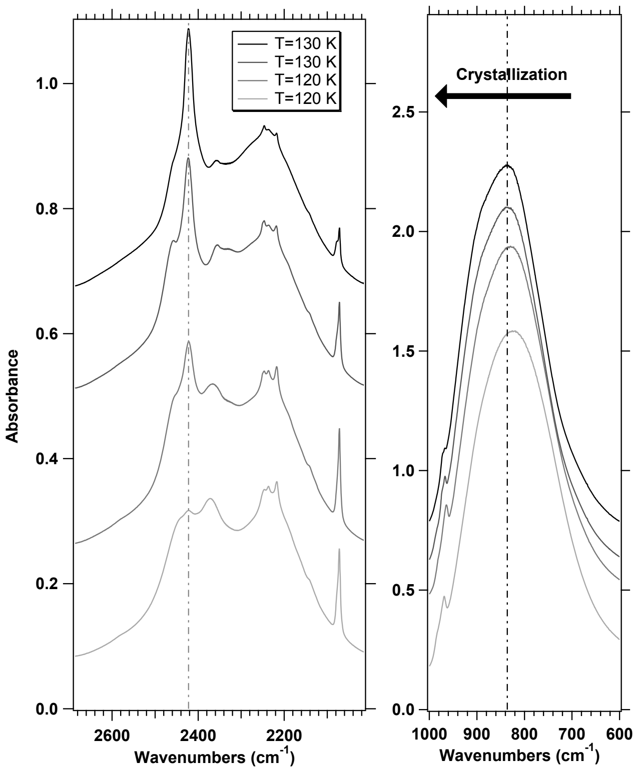

Fig. 2. Second experiment (110–130 K). *Left*: the isotopic H/D exchange between H_2O and the hydroxyl functional group of CD_3OD is traced by the HDO ν_{OD} band at 2425 cm^{-1}. *Right*: the libration water ice mode ν_L, used as a tracer of the crystalline state. H/D exchange occurs before the completion of crystallization. Spectra are vertically offset to ensure clarity in the figure.

HDO appeared as a band peaking at 2425 cm^{-1}, growing with increasing time and heating (left panel of Fig. 2). The librational water mode ν_L, which is a tracer of the crystalline state (Hagen & Tielens 1982), was used to indicate that i) water ice has experienced the phase transition (Ial) → (Ic) at 120 K and that ii) this phase transition was not completed when the H/D exchange was significantly advanced (right panel of Fig. 2).

Finally, it should be noted that besides the increasing intensity of the HDO ν_{OD} vibrational mode, in both experiments, complex spectral variations were observed in the spectra, including splitting, peak shifting, and variations in band intensities. It is not the purpose of this Letter to discuss those spectral variations in detail. They are definitely controlled by a variety of factors, in particular the degree of crystallinity and the degree of clustering of CD_3OD molecules (Quirico & Schmitt 1997a,b).

4. Discussion

The deuteration and the formation process of methanol are major issues in interstellar chemistry. Current gas-phase models do not account for the synthesis of methanol (Garrod et al. 2006). Therefore, formation routes onto and/or inside the icy mantles of interstellar grains have been proposed. Photolysis and radiolysis experiments of interstellar ice analogs show that methanol is efficiently formed from CH_4:H_2O or CO:H_2O mixtures (Hudson & Moore 1999; Wada et al. 2006). However, it is uncertain that such photolysis/radiolysis solid-state chemistry produces high H/D fractionation. In particular, the HDO/H_2O ratio of water ice is very low (Parise et al. 2003; Dartois et al. 2003) and the deuteration of CH_4 or CH_3^+ species is mostly unknown. Another possible chemical route is the reaction of D atoms at the surface of the grains, coming from a D-rich atomic gas produced by gas-phase chemistry fractionation (D/H ~ 0.1) (Watanabe & Kouchi 2002; Nagaoka et al. 2005). As mentioned in the Introduction, the experiments of Nagaoka et al. (2005) have demonstrated that singly, doubly, and triply deuterated methanol isotopologues, with D atoms located in the methyl group, can be produced via H-D substitution in solid methanol.

Our experiments are complementary to these works, as they have focused on the loss of deuterium in ice mixtures, i.e. a solid-state depletion mechanism. They clearly demonstrate that H/D exchange between the hydroxyl group of CD_3OD and H_2O necessarily occurs when ices are heated above 120 K, during the crystallization of water. It should be noted that thermally activated H/D exchange between D_2O and CH_3OH had been observed previously by Kawanowa et al. (2004) at temperatures above 140 K, often described as a critical temperature. We also note that some controversy exists in the detailed mechanism of the H/D exchange (see e.g., Lee et al. 2007, and references therein). In our experiments, exchange was found to occur only in intimate molecular mixtures, i.e. in couples of molecules spatially closely related. We thus conclude that long scale proton diffusion is kinetically hampered at $T < 170$ K (at least on a laboratory time scale), and that the key role of crystallization is to promote mobility, hence connections among –OH functions through hydrogen bonds. Astrophysically, this H/D exchange might explain the relative abundances of deuterated isotopologues of methanol, at least in low-mass protostellar sources (Parise et al. 2004, 2006). It does not exclude the formation of -OD methanol isotopologues on or in the grains, but suggests that D atoms located in the hydroxyl group of methanol should exchange with protons from ice. From this point of view, it is consistent with the presence of CH_3OD species in star-forming regions, while these are undetected in the experiment of Nagaoka et al. (2005). Moreover, the level of deuteration of H_2CO in low-mass protostars is similar to that of the methyl group of CH_3OH (Parise et al. 2006). This is also consistent with that fact that, in contrast to –OD functions, –CD functions do not exchange with H_2O.

In astrophysical conditions, this general mechanism might occur at lower temperatures owing to long time scales. In 10^5 years, the complete crystallization could occur at temperatures as low as 90 K (Schmitt 1992). Furthermore, proton mobility and thus isotopic exchanges may be triggered at even lower temperatures, without crystallization, during the progressive and partial structural reorganization of amorphous ice occurring during warmup above the condensation temperature (Schmitt et al. 1989). Definitely, systematic studies on CD_3OD:H_2O ice mixtures are required to provide more quantitative data. Other factors may also play a key role. The CH_3OH:H_2O ratio, which can be very high in some protostellar sources (Pontoppidan et al. 2003; Dartois et al. 1999), might limit the H/D exchange because CH_3OD molecules could be protected by others and could therefore avoid close interactions with H_2O. Such segregation effects have been suggested by comparing spectra of massive protostars with laboratory data (Ehrenfreund et al. 1998). In contrast, other effects could promote the H/D exchange by producing free protons, e.g. photolysis, radiolysis or dopants (Johari 2002). Finally, since this depletion mechanism occurs through the hydrogen bond, other detected molecules like deuterated isotopologues of ammonia could also exchange deuterium atoms with water ice if they experience some residence time on icy grains.

5. Conclusions

In this Letter, thin films of intimate H_2O:CD_3OD ice mixtures condensed at a low temperature (<110 K) have been investigated by FTIR spectroscopy up to the complete evaporation of CD_3OD (~170 K). It has been demonstrated that i) rapid H/D exchange between solid H_2O and CD_3OD occurs at temperatures as low as 120 K and before the completion of crystallization and ii) H/D exchange takes place on the hydroxyl functional group of methanol, through hydrogen bonds. These results suggests that the much lower abundance of CH_3OD compared to CH_2DOH in low-mass class 0 protostars might simply reflect H/D spontaneous exchange either prior to or definitely during the grain mantle sublimation. This solid-state depletion mechanism, so far neglected in the astronomical literature, might affect other deuterated molecules with hydrogen bonds (e.g. ND_3, N_2D^+). This will be explored in future works, both in the laboratory and at the telescope.

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