The Astrophysical Journal, 686:1474–1479, 2008 October 20

LABORATORY EVIDENCE FOR EFFICIENT WATER FORMATION IN INTERSTELLAR ICES

S. Ioppolo, H. M. Cuppen, C. Romanzin, E. F. van Dishoeck, and H. Linnartz
Raymond and Beverly Sackler Laboratory for Astrophysics, Leiden Observatory, Leiden University,
P.O. Box 9513, 2300 RA, Leiden, Netherlands
Received 2008 April 16; accepted 2008 June 30

ABSTRACT

Even though water is the main constituent in interstellar icy mantles, its chemical origin is not well understood. Three different formation routes have been proposed following hydrogenation of O, O_2, or O_3 on icy grains, but experimental evidence is largely lacking. We present a solid state astrochemical laboratory study in which one of these routes is tested. For this purpose O_2 ice is bombarded by H or D atoms under ultrahigh vacuum conditions at astronomically relevant temperatures ranging from 12 to 28 K. The use of reflection absorption infrared spectroscopy (RAIRS) permits derivation of reaction rates and shows efficient formation of H_2O (D_2O) with a rate that is surprisingly independent of temperature. This formation route converts O_2 into H_2O via H_2O_2 and is found to be orders of magnitude more efficient than previously assumed. It should therefore be considered as an important channel for interstellar water ice formation as illustrated by astrochemical model calculations.

Subject headings: astrochemistry — infrared: ISM — ISM: atoms — ISM: molecules — methods: laboratory

Online material: color figures

1. INTRODUCTION

Solid water ice has been observed on the surfaces of many different astronomical objects. In the solar system it is found on planets and minor bodies such as comets, trans-Neptunian objects, and Centaurs. In dense, cold interstellar clouds, infrared observations show that interstellar dust grains are covered with water-rich ices (e.g., Gillett & Forrest 1973; Gibb et al. 2004; Pontoppidan et al. 2004). The formation of these ice mantles is especially important in the process of star and planet formation, when a large fraction of heavy elements can be depleted onto grains. In the dense cloud phase water layers form on the bare grain surfaces. Then during the gravitational (pre)collapse, virtually all gas phase species freeze out on top of these water layers, resulting in a CO dominated layer that likely also contains traces of O_2 but very little water.

The observed H_2O ice abundance cannot be explained by direct accretion from the gas phase only. The exact mechanism by which water ice is formed is not understood. The *Herschel Space Observatory*, to be launched in the near future, will provide important new information on gaseous water in interstellar space and will measure quantitatively the water abundance as a function of temperature, UV field, and other parameters. Furthermore, the Photodetector Array Camera and Spectrometer (PACS) on *Herschel* will cover the 62 μm band of solid H_2O. In this way *Herschel* will provide a unique opportunity to observe the bulk of the water bands that are unobservable from the ground and relate them to *Spitzer* and ground-based mid-IR observations of ices in protostellar envelopes and protoplanetary disks. Understanding the processes by which water forms and why it is not formed under other circumstances will be essential for the interpretation of these data.

Tielens & Hagen (1982) proposed a reaction scheme in which water ice is formed on the surfaces of grains via three different routes: hydrogenation of O, O_2, and O_3. Models predict that water can indeed be formed through such reactions in dense clouds (e.g., Tielens & Hagen 1982; d'Hendecourt et al. 1985; Hasegawa & Herbst 1993; Cuppen & Herbst 2007). Using a Monte Carlo approach, Cuppen & Herbst (2007) showed that the contributions of the different formation channels to water ice formation as well as its abundance strongly depend on the local environment. However, the initial reaction scheme with the corresponding rates as proposed by Tielens & Hagen (1982) is based on old, in some cases outdated, gas phase data of the equivalent reactions. Progress has been severely hampered by the lack of realistic experimental simulations of these low-temperature, solid state reactions. Preliminary laboratory studies of water synthesis testing the first reaction channel have been reported by Hiraoka et al. (1998) and by Dulieu et al. (2007). Both groups investigated the products of D and O reactions on an ice substrate (N_2O and H_2O, respectively) using temperature programmed desorption (TPD). In experiments exclusively using this technique, it is hard to rule out any H_2O formation during warm up. Furthermore, quantitative interpretation can be tricky because unstable species such as H_2O_2 are destroyed in the mass spectrometer on ionization, leading to an artificially enhanced H_2O/H_2O_2 ratio.

The present work focuses on the H + O_2 channel in which O_2 is converted to H_2O via H_2O_2:

$$H + O_2 \rightarrow HO_2 \quad (1)$$

$$H + HO_2 \rightarrow H_2O_2 \quad (2)$$

$$H + H_2O_2 \rightarrow H_2O + OH \quad (3)$$

$$H + OH \rightarrow H_2O \quad (4)$$

According to Cuppen & Herbst (2007), this channel is, together with the O_3 channel, responsible for water formation in cold, dense clouds. The exposure of O_2 ice to hydrogen and deuterium atoms is investigated by means of reflection absorption infrared spectroscopy (RAIRS) and TPD. These techniques allow one to determine formation yields and the corresponding reaction rates. The present work comprises a study of hydrogenation and deuteration reactions of O_2 ice for different temperatures between 12 and 28 K, i.e., up to the desorption temperature of O_2 (Acharyya et al. 2007). The formation of H_2O and H_2O_2 is observed at all temperatures. An optimum yield is found at 28 K.

2. EXPERIMENTAL

Experiments are performed using an ultrahigh vacuum setup ($P < 5 \times 10^{-10}$ mbar) which comprises a main chamber and an

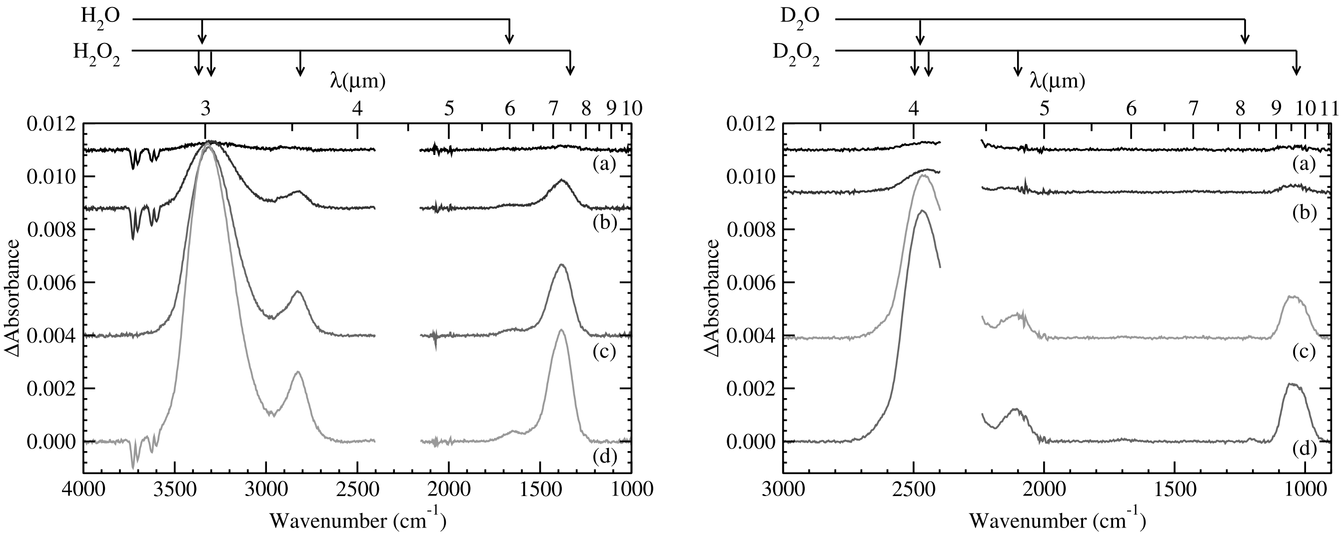

FIG. 1.—RAIR spectral changes of the O_2 ice as a function of H-atom (*left*) and D-atom (*right*) bombardment at 25 K. Spectra at a H(D)-atom fluence of (*a*) 4×10^{15}, (*b*) 4×10^{16}, (*c*) 1×10^{17}, and (*d*) 2×10^{17} cm^{-2} are given. [*See the electronic edition of the Journal for a color version of this figure.*]

atomic line unit. The setup is discussed in more detail in Fuchs et al. (2008). The main chamber contains a gold-coated copper substrate (2.5×2.5 cm^2) that is in thermal contact with the cold finger of a 12 K He cryostat. The temperature can be varied with 0.5 K precision between 12 and 300 K. A precision leak valve is used to deposit O_2 (99.999% purity, Praxair) on the substrate. Ices are grown at 45° with a flow of 1×10^{-7} mbar s^{-1}, where 1.3×10^{-6} mbar s^{-1} corresponds to 1 Langmuir (L) s^{-1}. In order to compare results from different experiments, the thickness of the O_2 ice is 75 L for all samples studied and the substrate temperature is kept at 15 K during the deposition. An O_2 ice of 75 L consists of roughly 30 monolayers. This thickness is chosen to exclude substrate-induced effects. Because a diatomic homonuclear molecule like O_2 is infrared inactive, gas-phase O_2 is monitored during the deposition by a quadrupole mass spectrometer (QMS). After deposition at 15 K the ice is slowly cooled down or heated (1 K minute^{-1}) until a selected temperature is reached. Systematic studies are performed for different temperatures between 12 and 28 K.

H(D) atoms are produced in a well-characterized thermal-cracking device (Tschersich & von Bonin 1998; Tschersich 2000). A second precision leak valve is used to admit H_2 (D_2) molecules (99.8% purity, Praxair) into the gas cracking line. In each experiment the $H + H_2$ ($D + D_2$) flow through the capillary in the atomic line is 1×10^{-5} mbar s^{-1} and the temperature of the heated tungsten filament, which surrounds the gas cracking pipe, is about 2300 K. The dissociation rate and the atomic flux depend on the pressure and temperature (Tschersich 2000), and are kept constant during all the experiments. A nose-shaped quartz pipe is placed along the path of the atomic beam in order to cool down H (D) atoms to room temperature before reaching the ice sample by collisions (Walraven & Silvera 1982). The H (D) atomic flux nearby the sample is estimated, within 50%, as 5×10^{13} cm^{-2} s^{-1}. At temperatures of 12 K and higher, no blocking of surface processes by the presence of H_2 is expected in the ice.

The newly formed species after hydrogenation (deuteration) of O_2 ice are monitored by RAIRS using a Fourier transform infrared spectrometer (FTIR) running at a spectral resolution of 4 cm^{-1} in the range between 4000 and 700 cm^{-1} (2.5–14 μm). Typically the ice is exposed to the H (or D) beam for 3 (or 2) hr and IR spectra are acquired every few minutes.

Systematic control experiments have been performed in order to (1) unambiguously confirm that the products are formed by surface processes and not by gas phase reactions, (2) check that any water present in the system does not affect the final results, and (3) verify that water and H_2O_2 formation occurs in the solid phase after H (D)-atom bombardment and not by H_2 (D_2) molecule addition. For (1), codeposition experiments are undertaken in which H and O_2 are deposited simultaneously. H_2O_2 is only formed if the surface temperature is below the desorption temperature of oxygen, confirming that the presence of the oxygen ice is required for this reaction sequence to occur. Point (2) is verified by using inert initial substrates such as N_2 ice to estimate the background water contribution, as well as by using different isotopologues ($^{18}O_2$, $^{15}N_2$, and D). Finally, (3) is checked by using pure H_2 (D_2) beams, i.e., without any H (D) present.

3. RESULTS

The formation of both H_2O_2 and H_2O ice is confirmed by the appearance of their infrared solid state spectral signatures. Figure 1 shows typical RAIRS results for hydrogenation and deuteration of O_2 ice at 25 K. From top to bottom a time sequence of four spectra is plotted. These spectra are difference spectra with respect to the initial oxygen ice. However, since our initial oxygen ice only consists of 30 ML, no features due to the intrinsically very weak O_2 feature (Ehrenfreund et al. 1992; Bennett & Kaiser 2005) are observed in the original spectrum. Both the H_2O and H_2O_2 clearly grow in time as the H-fluence (H flux × time) increases. Similar features appear for the deuteration experiment, although here clearly less D_2O is formed. After fitting the infrared spectra with a straight baseline, the column density (molecules cm^{-2}) of the newly formed species in the ice is calculated from the integrated intensity of the infrared bands using a modified Lambert-Beer equation (Bennett et al. 2004). In the range of our spectrometer, water ice has two candidate bands for determining its column density, at 3430 and 1650 cm^{-1} (3 and 6 μm, respectively). Since the strong 3430 cm^{-1} feature overlaps with the 3250 cm^{-1} band of H_2O_2, the weak feature at 1650 cm^{-1} was chosen to quantify the water column density. Since literature values of transmission band strengths cannot be used in reflection measurements, an apparent absorption strength is obtained from a calibration experiment in which a pure water ice layer desorbs at constant temperature until the submonolayer regime (Öberg et al. 2007). The uncertainty in the band strengths remains within a factor of 2. Quantification of H_2O_2 is done using the 1350 cm^{-1} band. As it is experimentally