

Dr. Curt Niebur
Outer Planets Research Program
Office of Space Science
NASA Headquarters
Washington, DC 20546-0001

Sept. 29, 2010

Dear Dr. Niebur,

You will find enclosed my final report for grant NNX07AM75G “Energetic Processing and Stimulated Chemistry of Pre-Cometary Ices and the Primordial Surfaces of Comet Nuclei.” Please let me know if any additional information is required.

Sincerely,

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Final Report

NASA Outer Planets Research Program “Energetic Processing and Stimulated Chemistry of Pre-Cometary Ices and the Primordial Surfaces of Comet Nuclei”

Program: NNX07AM75G

**Thomas M. Orlando, Principal Investigator
For the period 04-June-2007 - 03-June-2010**

1. Program Objectives

Comets are regarded as the most pristine samples from the formation of our solar system. Their elemental abundances, isotope ratios and ortho-para spin temperatures contain information concerning the composition and dynamics of the early evolution of the solar system. This program provided further information on the physics and chemistry involved in the radiation processing and stimulated chemical reactions within pre-cometary ices and in the outer layer of current comet nuclei. During the period of grant NNX07AM75G, we examined the following issues: What are the detailed dynamics of isotopic substitution on fast electronic dissociation and hot-atom reactive scattering events in ice and mixed ices? What is the role of carbonaceous grains on deuterium isotope fractionation and selective ortho-para spin adsorption and interconversion? Are there mechanisms in electronic dissociation that are nuclear-spin state selective? These effects in cometary ice over long periods may alter the apparent composition and hence affect the accuracy of extrapolation backward to the origins of comets and our solar system.

2. Summary of Progress

Task 1. ELECTRON BEAM INDUCED FORMATION OF ATOMIC OXYGEN AND MOLECULAR HYDROGEN

We have used resonance enhanced multiphoton ionization to detect the atomic oxygen and molecular hydrogen produced during electron beam irradiation of low temperature, porous amorphous ice. These products are produced by a complicated dissociation involving the lowest exciton ($4a_1^1$) of ice. Figure 1 and 2 show the yield of the H_2 ($^1\Sigma_g^+$) $O(^3P_1)$ as a function of the ice phase and porosity. The initial rise and decay of the oxygen atom yield between 90 and 130 K is related to pore collapse and sintering of the ice. The

large yield of both the oxygen and hydrogen at 150 K is related to an increased lifetime of the exciton associated with reduced hydrogen bonding and increased hydrogen-bond distances at temperatures above 135 K. We have also previously shown that these changes in the ice also allow rapid release of trapped molecules such as H₂ and O₂.

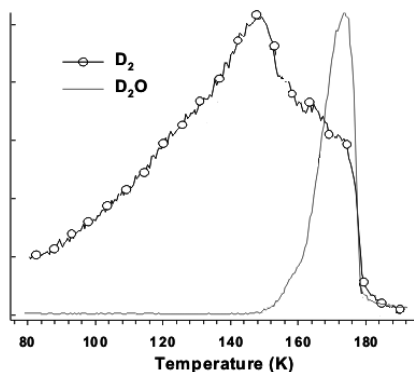


Figure 1. Temperature dependence of production of molecular hydrogen (D₂) from electron irradiated D₂O ice. The open circles is the stimulated production of D₂. The solid lines is the temperature programmed desorption of D₂O. Simialr results are also observed for O and O₂. (See below). The strong correlation indicates a connection in the source term.

The production of O₂ and H₂ (D₂) from low temperature ices follow the same energy threshold and temperature dependence as the yield of O (³P₁). The fact that molecular hydrogen forms in a direct molecular elimination step allows us to map out the spin-state distributions.

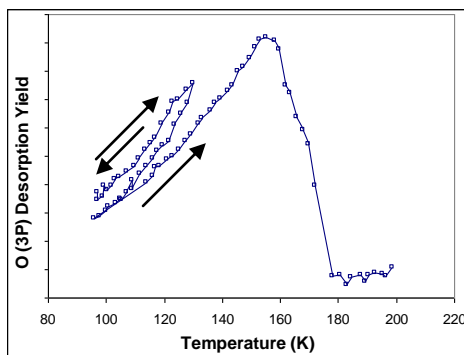


Figure 2. The temperature dependence of the O (³P₁) measured by (2+1) resonance multiphoton ionization, produced and released during electron (100 eV) bombardment of low-temperature amorphous ice. The initial curve shows enhanced production followed by hysteresis due to sintering of pores from 100 to 120 K.

Task 2. STATE-RESOLVED SPIN DISPROPORTIONATION

We used laser resonance enhanced multiphoton ionization (REMPI) to map out the ortho/para distribution of the hydrogen below in Figure 3.

produced and released during the pulsed irradiation of the water covered surface. An example of the state-resolved data for the stimulated production and removal of D₂ is shown

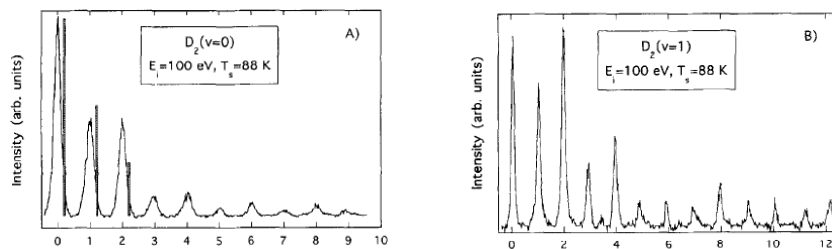


Figure 3. Intensity versus rotational quantum number for (A) D_2 ($v=0$) and (B) D_2 ($v=1$) produced via electron beam impact of ice at 88 K. Even J states are only allowed for ortho- D_2 ($I = 0, 2$) whereas odd J states are only allowed for para- D_2 ($I = 1$) as a result of Pauli exclusion. The observed OPR is equal to that of the ice, not the OPR of D_2 at 88 K. (G. A. Kimmel, R. G. Tonkyn, and T. M. Orlando, Nucl. Instr. & Methods in Physics Research: Beam Interactions with Materials and Atoms **101**, 179 (1995)).

The H_2 (D_2) is produced via a direct elimination channel and is *not* produced in substantial quantities on the time scale of these measurements by recombinative desorption. This is a very important since it allows us to probe the presence of ortho and para water by analyzing the ortho and para state distributions of the resultant molecular hydrogen. The data shown above was taken using multilayers at 88K. The known nuclear spin temperature dependence, T_{spin} , of H_2O and H_2 are shown in Figure 4. Hydrogen has a more gradual dependence on temperature than water due to the lower density of states of rotational levels.

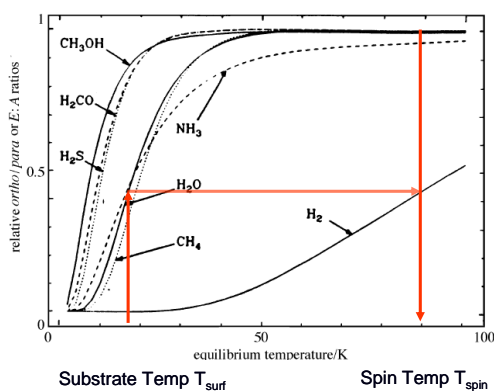


Figure 4. Plot of relative ortho para ratios for selected hydrogenic molecules. Our measurement of H_2 production by direct dissociation of H_2O shows that the ortho-para spin temperature carries information about the ice substrate temperature.

We have fit our data shown in Figure 3 using Boltzmann functions to describe the rotational temperature (T_{rot}), multiplied by the rotational level degeneracy ($2(J+1)$), the nuclear spin state degeneracy $U_{o,p}$ and the ortho para population $X_{o,p}(T_{\text{spin}})$ for molecules in spin equilibrium at the temperature they are created.

$$I_{o,p} = U_{o,p} X_{o,p}(T_{spin}) (2J+1) [\Sigma C_n(J, T_{rot})]$$

Figure 5 shows the fits to this function for the D₂ data taken at a substrate temperature of 88 K. The fits were made using contributions from two distinct components, the first with 95% T_{rot} = 100 K and an O:P ratio corresponding to T_{spin} = 76 K, the second 5% with T_{rot} = 1500 K and T_{spin} = 195 K. This indicates that the majority of the hydrogen generated is in near spin equilibrium with the substrate, but for the minority component, the internal rotational temperature is extremely hot but T_{spin} corresponds to the spin equilibrium for the ice substrate itself (see Figure 4). Thus, if D₂ is ejected by direct unimolecular dissociation at the vacuum interface, it carries information about the D-D internuclear separation of the ice surface that produced it.

Task 3. IS THERE ISOTOPE FRACTIONATION IN STIMULATED DISSOCIATION?

We have examined isotope fractionation in the electron-stimulated damage of water. Our data, shown below in Figure 5, indicates that the amount of D⁺ relative to H⁺ sputtered directly from ice increases with increasing excitation energy, particularly for high-temperature ice.

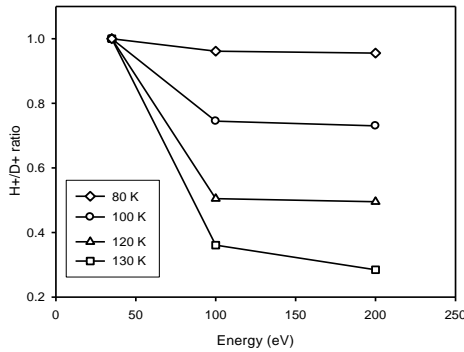


Figure 5. Plot of normalized H⁺/D⁺ ratio from low-energy electron bombarded mixed H₂O, D₂O ice on a graphite substrate. The ratios vary according to the excitation energy of incident electrons. The amount of sputtered H⁺ drops in comparison to D⁺ with increasing energy. The dependence also varies with temperature and is more pronounced for warmer ices (130 K, ■ ◆) vs cold ice (80 K, ◆).

These results are opposite to the isotope effect observed in the electron-impact induced production of D₂⁺ (H₂⁺) from gas-phase water and also differs somewhat from the electron impact production of D⁺ (H⁺) from gas-phase water where there is little isotope effect observed. Thus, there are important differences associated with the condensed phase which can lead to strong isotope effects in radiation induced damage of ice.

Task 4. EXAMINE DIFFERENTIAL ISOTOPE FRACTIONING INVOLVING ORGANIC SPECIES AND HYDROGEN TERMINATED CARBONACEOUS SUBSTRATES.

An important element of this program was to examine the role of the substrate and interfacial energy or charge exchanges on the stimulated desorption and reaction cross sections. The electronic structure of the substrate interface and coupling to adsorbed water affects the radiolytic decomposition channels that result in hydrogen and oxygen production. We have also found that an oxidizable substrate such as graphite can interfere with the sequential process of generating oxygen precursors and consume them, while simultaneously generating CO and CO₂.

Figure 6 shows the rich spectra of ion products desorbed from a clean graphite surface which contains trace amounts of water. The substrate temperature was 45 K. Electron irradiation ejects carbon-containing ionic fragments into the gas-phase; however, there are also higher mass hydrocarbons and oxygen containing products which clearly arise from the substrate and reactive scattering events.

Since ices in nature rarely occur in pristine form, studies of the effect of trace amounts of co-deposited species and inclusions of carbonaceous dust grains are needed to fully compare laboratory measurements to real systems. We have found that the presence of organic small molecules significantly affects the reaction sequence that normally results in O₂ generation.

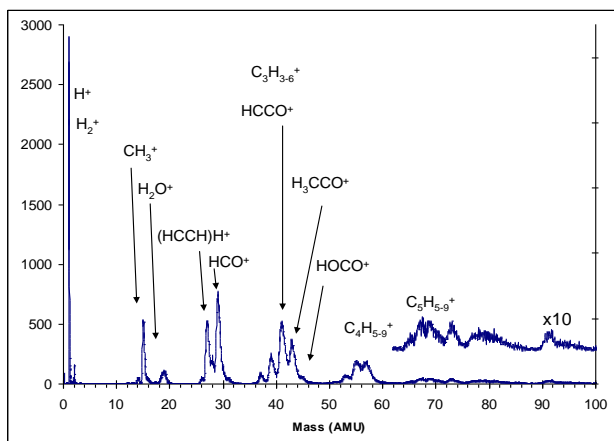


Figure 6. Time of flight mass spectra of ions produced and desorbed from electron irradiation of graphite surfaces containing trace amounts of water and oxygen. Note the formation of higher mass hydrocarbons and the formation of oxygen containing products.

The above studies on the detailed mechanism of stimulated production and desorption non-thermal products from ice have been extended to include co-adsorbed

CH₄ and other small molecules observed in cometary ices, the interstellar medium and outer solar system. Figure 7 presents the results of stimulated production of CO₂ during the irradiation of H₂O ice containing CH₄ trapped in micropores. The release of CO₂ occurs at 170K which is commensurate with the amorphous-to cubic phase transition.

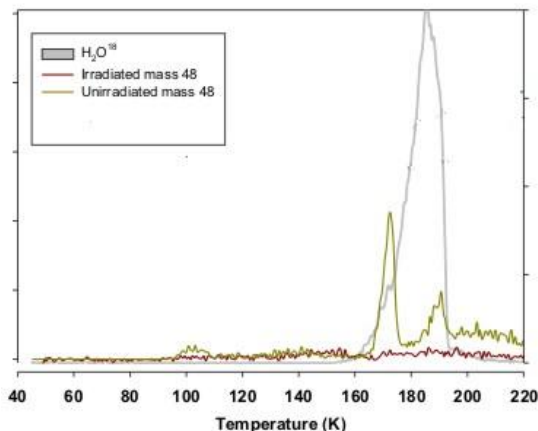


Figure 7. Post-irradiation thermal desorption spectrum of O¹⁸ isotope labeled CO₂ generated from irradiation of organically doped ice.

Task 5. TEMPERATURE PROGRAMMED DESORPTION OF MIXED CO₂ AND WATER ICE

Finally, we have collaborated with Prof. Perry Gerakines (another PI in the NASA OPR program) at the Department of Physics, University of Alabama, on understanding the optical signatures and release rates of CO₂ trapped in low temperature water ice. We observe a useful correlation of the IR signal and thermal release of CO₂ with the microporosity of the ice. This is largely due to sintering/pore collapse at temperatures below 120K. The major release occurs in the form of a molecular “volcano” during the amorphous-to-cubic phase transition at 145K. This rapid release occurs due to the open percolation paths associated with the large structural changes in ice during nucleation and crystal growth from an initially amorphous state of ice. This can be considered a general driving force for the outgassing of comets. This work was published as part of D. White’s Ph.D. thesis and a paper submitted to the J. of Physical Chemistry.

Publications and Presentations:

Orlando, T.M., and Grieves, G.A., “The formation and fate of oxidants on icy satellite surfaces.” Fall AGU December 2007.

Orlando, T. M. , “The Roles of Energy Localization and Buried Interfaces in Electronic Sputtering of Pristine and Mixed Low-temperature Ices”, The Science of Solar System Ices (ScSSI): A Cross-Disciplinary Workshop, Ventura, CA May 5-8, 2008.

Grievess, G.A., and Orlando, T.M. “Low energy electron-induced desorption from low temperature ices and outer solar system surfaces,” Contributed Talk, DIET XII, Pine Mountain GA, April 19-23, 2009.

Orlando, T. M. “Quantum-resolved Studies of Stimulated Processes in Complex Ice Mixtures and at Grain Surfaces”, Southeast Association for Laboratory Astrochemistry (SELAC)’, Invited talk, Athens, GA, March 30, April 1, 2010.

Hibbitts C. A. * Dyar M. D. Orlando T. M. Grievess G. Moriaty D. Poston M. Johnson A. “Thermal stability of water and hydroxyl on airless bodies”, Lunar Planet. Sci. 41, abstract 2417 (2010).

White, D. W., Gerakines, P., Grievess, G. , and Orlando, T. M. “An IR and Temperature Programmed Desorption Study of Low-temperature CO₂ : H₂O Ices”, J. Phys. Chem. A.

Grievess, G. A., Shepperd, K., and Orlando, T. M. “Low-energy electron-stimulated oxidation of low temperature water ice covered graphite surfaces”, Astrophys. J. Lett. (*submitted*)

Grievess, G.A. and Orlando, T.M., “Stimulated reactions on graphite grains and interfaces: A source for CO, HCO and H₂CO,” Chem. Phys. Lett. (*in prep.*)

Grievess, G.A. and Orlando, T.M., “Stimulated production and release of CO₂ from electron irradiated CH₄:H₂O Ices,” Ap. J. Lett. (*in prep.*)

Grievess, G.A., Orlando, T.M. “Rotational and Spin Temperature Disproportionation of Molecular Hydrogen Produced From Low Temperature Ices,” Astrophys. J, (*in prep.*)