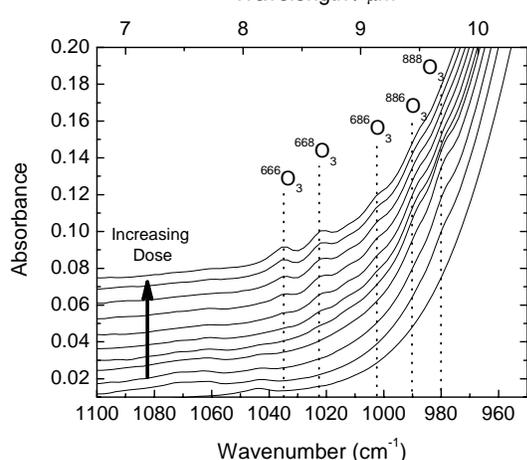


**THE SYNTHESIS AND DIRECT DETECTION OF O-ATOMS IN WATER ICE.** P. D. Cooper<sup>1</sup>, M. H. Moore<sup>2</sup> and R. L. Hudson<sup>3</sup>, <sup>1</sup>Department of Chemistry and Biochemistry, MS 3E2, George Mason University, 4400 Universtry Drive, Fairfax, VA 22030, pcooper6@gmu.edu <sup>2</sup>NASA/Goddard Space Flight Center, Astrochemistry Branch, Code 691, Greenbelt, MD 20771, Marla.H.Moore@nasa.gov <sup>3</sup>Department of Chemistry, Eckerd College, 4200 54th Avenue South, St. Petersburg, FL 33711, hudsonrl@eckerd.edu

**Introduction:** There have been several recent laboratory investigations of the formation of molecular oxygen from irradiated water ice [1-3]. This is of particular interest in the formation of O<sub>2</sub> on the surface of the icy Galilean satellites [4-5] and also an O<sub>2</sub> atmosphere associated with Saturn's rings [6-7]. Both sources of O<sub>2</sub> are postulated to be formed from the radiolytic and/or photolytic destruction of H<sub>2</sub>O molecules in the ice grains of these objects.

**Experimental:** In brief, we prepare gaseous mixtures of H<sub>2</sub>O + <sup>18</sup>O<sub>2</sub> (6:1) in a vacuum manifold. Millipore water was freeze-pump-thaw cycled multiple times to remove dissolved atmospheric gases. The <sup>18</sup>O<sub>2</sub> (Isotec; purity of >97%) was used without further purification. Blank experiments on irradiated pure <sup>18</sup>O<sub>2</sub> produced <sup>18</sup>O<sub>3</sub> and no other detectable isotopologues. The H<sub>2</sub>O + <sup>18</sup>O<sub>2</sub> gaseous mixtures were then deposited onto an aluminum mirror, cooled to 10 K by a closed-cycle helium refrigerator. The samples are then warmed to 80 K at ~2 K/min. An increase in the vacuum chamber base pressure at ~30 K indicates that some of the O<sub>2</sub> sublimates out of the ice. This is consistent with previous work [8]. Due to the sublimation of some of the O<sub>2</sub>, the exact H<sub>2</sub>O to O<sub>2</sub> ratio is unknown. The samples are then irradiated with 0.8 MeV protons generated from a Van de Graaff accelerator. IR spectra are measured using a Nicolet 6700 Nexus spectrometer at 4 cm<sup>-1</sup> spectral resolution.

**Results:** The figure below shows spectra of a



6:1 H<sub>2</sub>O + <sup>18</sup>O<sub>2</sub> sample with increasing radiation dose. As the dose increases a broad but shallow

absorption band appears at 980 and 990 cm<sup>-1</sup> associated with the formation of the 888 and 886 isotopologues, where 8 represents an <sup>18</sup>O atom and 6 represents a <sup>16</sup>O atom. The 888 is produced from residually trapped <sup>18</sup>O<sub>2</sub> molecules that are nearest neighbors. The irradiation of pure <sup>18</sup>O<sub>2</sub> did not yield any measurable ozone isotopologues containing <sup>16</sup>O and there is no measurable amount of CO<sub>2</sub> atmospheric contaminant in our sample. The <sup>16</sup>O atom in the 886 must originate from H<sub>2</sub>O. The 888 species is gradually destroyed with increasing dose by the replacement of <sup>18</sup>O by radiolytically-produced <sup>16</sup>O to form 886.

We have considered the possibility that the source of <sup>16</sup>O in these experiments could be from <sup>16</sup>OH formed in the radiolytic destruction of H<sub>2</sub>O. An ozone molecule containing a <sup>16</sup>O atom could then be formed by the following reactions.



However, calculations [9] show that this reaction probably does not occur to any great extent. The HO<sub>3</sub> intermediate is only marginally below the OH + O<sub>2</sub> state on the ground state HO<sub>3</sub> potential energy surface. These workers have shown that the O + HO<sub>2</sub> and H + O<sub>3</sub> states are accessible in the gas-phase when the reacting O<sub>2</sub> and OH are in highly excited vibrational states. These excited states are likely to be very rapidly quenched in the cold ices in discussion in the present work.

**Conclusions:** Using a band strength of 1.4 x 10<sup>-17</sup> cm molecule<sup>-1</sup> for the ν<sub>3</sub> band of O<sub>3</sub>, and assuming that it is the same for all isotopologues, we have calculated that there is 0.14% O atoms by number relative to H<sub>2</sub>O at the highest dose of 9.8 eV/16-amu molecule. In pure water ice, without the presence of <sup>18</sup>O<sub>2</sub> to trap the <sup>16</sup>O atom as an ozone isotopologue, it could be argued that the highly reactive <sup>16</sup>O atom may react with water or another water radiation fragment (such as H or OH) before ever encountering a second radiolytically produced <sup>16</sup>O atom. If the ozone isotopologues produced in the present work were dissociated and the <sup>16</sup>O atoms were to reform exclusively as <sup>16</sup>O<sub>2</sub>, then there would be 0.07% O<sub>2</sub> by number, relative to H<sub>2</sub>O. This small amount of O<sub>2</sub> is far beyond the detection limits of our spectrome-

ter in pure water, but using the O<sub>3</sub> tracer molecule, we can detect the O atom production which would otherwise form O<sub>2</sub>.

It is common in radiation chemistry to present production rates as a yield,  $G$ , the number of molecules produced per 100 eV of energy absorbed. We have calculated an effective  $G_{H^+}(^{16}O)$  (calculated from the number of <sup>16</sup>O atoms measured in ozone isotopologues) to be 0.013. Again however, this value represents a lower limit due to the O atoms that cannot be directly measured in this experiment and it is only an effective G-value as we are actually not measuring <sup>16</sup>O atoms directly, but indirectly in the form of ozone isotopologues.

Estimates of the O<sub>2</sub> abundance on Ganymede range from 0.1 - 1.0% [10] to 1.4 - 4.2% [11]. While our percentage abundance is lower than these estimates, our value represents a lower limit estimate that is in good agreement with the observations.

**References:** [1] Orlando T. M. and Sieger M. T. (2003) *Surf. Sci.* 528, 1-7. [2] Petrik N. G. et al. (2006) *J. Phys. Chem. B* 110, 2723-2731. [3] Teolis B. D. et al. (2006) *Astrophys. J.* 644, L141-L144. [4] Spencer J. R. et al (1995) *JGR* 100, 19,049-19,056. [5] Spencer J. R. and Calvin W. M. (2002) *Astrophys J.* 124, 3400-3403. [6] Tokar R. L. et al. (2005) *GRL* 32, L14SO4; [7] Johnson R. E. et al. (2006) *Icarus* 180, 393-402. [8] Loeffler M. J. et al. (2006) *Astrophys J.* 639 L103-L106. [9] Yu H. G. and Varandas A. J. C. (2001) *Chem. Phys. Lett.* 334, 173-178. [10] Calvin W. M. et al. (1996) *GRL* 23, 673-676. [11] Hand K. P. et al. (2006) *Astrobiology* 6, 463-482.