# Water at High Dynamic Pressures and Temperatures

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*Dedicated to Professor Gérard Demazeau on the occasion of his 65$^{th}$ birthday*

This paper is dedicated to Prof. G. Demazeau for his many contributions to the study of materials at high pressures and to the International Association for the Advancement of High-Pressure Science and Technology. This paper discusses two of Prof. Demazeau's interests, water and high pressures. Experimental measurements are reviewed for water compressed dynamically from pressures of a few GPa up to 1.4 TPa and temperatures from 100 K up to 50000 K.

*Key words:* Water, Chemical Ionization, Hugoniot, Multiple-shock Compression

## Introduction

Prof. G. Demazeau has been very active throughout his career in the international high-pressure community. He was Chairman of the 2003 *Conference of the International Association for the Advancement of High-Pressure Science and Technology* (AIRAPT) in Bordeaux, and he has served on the Executive Committee of AIRAPT. Much of his work has been concerned with synthesis of strong oxides at pressures up to 2 GPa (20 kbar) [1]. Recently, he was a member of the organizing committee of the 2007 International Workshop on Water Science and Technology. Water is a very important substance that has received much attention by the international high-pressure community. The purpose of this paper is to combine two of Prof. Demazeau's interests, water and high pressures, by reviewing measured properties of water compressed dynamically from a few GPa up to 1.4 TPa at temperatures from 100 K up to 50000 K.

Water is a fundamental molecule whose properties change dramatically with pressure, density, and temperature. It exists naturally in the forms of extremely low-density nebular gas and in the liquid and solid state on the surface of the Earth. At high pressures and temperatures water decomposes to form a dense chemically-ionized fluid. For example, the giant planets Uranus and Neptune accreted from massive amounts of nebular water, as well as other hydrogenous molecules, ammonia and methane. Because of the large gravitational masses and poor thermal conductivities of fluids in these planets, interior pressures and temperatures range up to several 100 GPa and several 1000 K.

Thermal energies comparable to intermolecular and intramolecular bond energies at ambient, $\sim 0.1$ and 0.6 eV, respectively, cause these bonds to break. In addition, intermolecular and intramolecular bond lengths of water at ambient are reduced by compression, which if sufficiently high breaks hydrogen bonds between molecules and chemically ionizes molecules, as well [2 – 4]. In this paper we consider application of pressure and temperature. Pressures and temperatures can be tuned independently in both static and dynamic compression experiments. Static pressure is applied by a press, and temperature is varied independently by heating or cooling the sample [5].

Dynamic compression pressurizes and heats a sample simultaneously. Temperature at a given pressure is tuned by tuning the time over which dynamic pressure is applied. A shock wave compresses a liquid quickly ($\sim 10^{-12}$ s), which causes temperature to be relatively high. An isentropic compression occurs slowly ($\sim 10^{-8}$ s), which causes temperature to be relatively low. Temperature at a given pressure is tuned dynamically by tuning the relative amounts of shock and isentropic heating [6].

The locus of states produced by a series of single shocks in a given material with a given initial density is called the Hugoniot of that material. Hugoniot experiments typically have a time resolution of 1 ns and a duration of 100 ns, sufficiently long to achieve ther-

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mal equilibrium and sufficiently short that shock compression is adiabatic. That is, the time scale is too fast for significant thermal transport in or out of the sample during the lifetime of the experiment. The same is true for dynamic isentropic compression. Single-shock temperatures can be relatively high and, thus, can limit density that can be achieved.

In contrast, multiple-shock compression traverses a series of thermodynamic states, which in total are called a quasi-isentrope. The first shock pressurizes and heats a sample to a point on its Hugoniot, and successive shocks compress the sample to higher pressures and densities essentially along an isentrope starting from the first-shock state. Compression along a quasi-isentrope is also adiabatic. Compression is not limited on quasi-isentropes. Dynamic compression describes compression by a single shock, multiple shocks, and by compression along an isentrope (no initial shock).

Because chemically ionized water is highly corrosive, possible effects of corrosion must be taken into account in the choice of experimental conditions of pressure, temperature, and their time durations. Corrosion is essentially negligible in dynamic compression experiments because experimental lifetimes, $\sim$100 ns, are too short for significant corrosion to occur. Experiments at long-lived static pressures and temperatures are generally limited to relatively low ionic fractions because of corrosion. Experiments at relatively high static pressures, temperatures, and ionic fractions are limited by the time at these conditions and/or by the necessity for non-corrosive materials to isolate chemically ionized water from its sample holder.

## Results and Conclusions

The first indication that water molecules chemically ionize at high pressures and temperatures was the Hugoniot data of Altshuler *et al.* which showed that water becomes more compressible above a shock pressure of 12 GPa and 800 K than it is below this shock pressure [7]. Water essentially retains its molecular nature and intermolecular hydrogen bonds under static pressures and temperatures up to 10 GPa and 1000 K [5]. The Grüneisen parameter of water goes through a maximum at a density corresponding to a shock pressure of 12 GPa [2, 8, 9], which indicates that at higher shock pressure energy is absorbed internally as well as thermally.

Raman scattering from shock-compressed water shows that the concentration of intermolecular hydrogen bonds begins to decrease at 12 GPa and that these bonds essentially vanish at 26 GPa. Only the $OH^-$ stretch band is observed in those experiments. At ambient conditions $H_2O$ has an estimated ionization fraction of $10^{-7}$ mol$^{-1}$. The resulting proton attaches itself to an $H_2O$ molecule to form $H_3O^+$. The spectral feature expected for $H_3O^+$ is not observed in shock-compressed $H_2O$, which means that the lifetime of $H_3O^+$ is less than the 10 ns experimental lifetime, and that protons formed by chemical ionization of water molecules are not bound in ions on this time scale [3].

In electrical conductivity experiments protons are generally considered to be the charge carriers in water compressed and heated by one or multiple shocks up to $\sim$ 180 GPa [2, 4, 5, 10, 11]. States achieved in [2, 4] lie on the isentrope of Neptune [12, 13]. Protons have negligible volume to easily diffuse through complex fluid water, and $H_3O^+$ is not observed in Raman scattering experiments [3]. Measured values of electrical conductivity are in good agreement with values calculated with a simple Drude model that assumes that carrier mass is the mass of a proton, the mean free path of a proton is the average distance between neighboring water molecules, and protons travel at thermal velocity. The electronic band gap of water is expected to close at 300 GPa and 7000 K [14]. Measurements of optical reflectivities of the shock front in samples precompressed to 1 GPa have shown that shocked water becomes electrically conducting above 130 GPa [12]. Some of these states are also on the isentrope of Neptune.

Single and double equation-of-state data were measured up to 80 and 220 GPa, respectively [2]. At a single-shock pressure of 80 GPa, the temperature is 5500 K [15]. At these conditions water is probably chemically ionized into $H^+$ and $OH^-$. At 1.4 TPa on the Hugoniot the density is 4 g cm$^{-3}$ and the estimated temperature $\sim$ 50000 K. In this regime electron thermal pressure is expected to be the major contribution to total pressure, and a simple Thomas-Fermi model is in reasonable agreement with the experiment [16].

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[1] G. Demazeau, *High Pressure Research* **2000** *18*, 203–212.

[2] A. C. Mitchell, W. J. Nellis, *J. Chem. Phys.* **1982**, *76*, 6273–6281.

[3] N. C. Holmes, W. J. Nellis, W. B. Graham, G. E. Walrafen, *Phys. Rev. Lett*. **1985**, *55*, 2433 – 2436.

[4] R. Chau, A. C. Mitchell, R. W. Minich, W. J. Nellis, *J. Chem. Phys*. **2001**, *114*, 1361 – 1365.

[5] W. Holzapfel, E. U. Franck, *J. Chem. Phys*. **1969**, *50*, 4424 – 4428.

[6] W. J. Nellis, *Rep. Prog. Phys*. **2006**, *69*, 1479 – 1580.

[7] L. V. Altshuler, A. A. Bakanova, R. F. Trunin, *Sov. Phys. Doklady* **1959**, *3*, 761 – 763.

[8] G. A. Gurtman, *J. Appl. Phys*. **1971**, *42*, 851 – 857.

[9] J. M. Walsh, M. H. Rice, *J. Chem. Phys*. **1957**, *26*, 815 – 823.

[10] S. D. Hamann, M. Linton, *Trans Faraday Soc*. **1966**, *62*, 2234 – 2241.

[11] S. D. Hamann, M. Linton, *Trans Faraday Soc*. **1969**, *65*, 2186 – 2196.

[12] K. K. M. Lee, L. R. Benedetti, R. Jeanloz, P. M. Celliers, J. H. Eggert, D. G. Hicks, S. J. Moon, A. Mackinnon, L. B. Da Silva, D. K. Bradley, W. Unites, G. W. Collins, E. Henry, M. Koenig, A. Benuzzi-Mounaix, J. Pasley, D. Neely, *J. Chem. Phys*. **2006**, *125*, 014701 – 014707.

[13] W. B. Hubbard, M. Podolak, D. J. Stevenson in *Neptune and Trition* (Ed.: D. P. Cruikshank), University of Arizona Press, Tucson **1995**, pp. 109 – 145.

[14] C. Cavazzoni, G. L. Chiarotti, S. Scandolo, E. Tossati, M. Bernasconi, M. Parrinello, *Science* **1999**, *283*, 44 – 47.

[15] G. A. Lyzenga, T. J. Ahrens, W. J. Nellis, A. C. Mitchell, *J. Chem. Phys*. **1982**, *76*, 6282 – 6286.

[16] M. A. Podurets, G. V. Simakov, R. F. Trunin, L. V. Popov, B. N. Moiseev, *Sov. Phys. JETP* **1972**, *35*, 375 – 379.