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Photoacoustically Measured Speeds of Sound of Liquid HBO$_2$: On Unlocking the Fuel Potential of Boron


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ABSTRACT Elucidation of geodynamic, geochemical, and shock induced processes is often limited by challenges to accurately determine molecular fluid equations of state (EOS). High pressure liquid state reactions of carbon species underlie physiochemical mechanisms such as differentiation of planetary interiors, deep carbon sequestration, propellant deflagration, and shock chemistry. Here we introduce a versatile photoacoustic technique developed to measure accurate and precise speeds of sound (SoS) of high pressure molecular fluids and fluid mixtures. SoS of an intermediate boron oxide, HBO₂, are measured up to 0.5 GPa along the 277 °C isotherm. A polarized Exponential-6 interatomic potential form, parameterized using our SoS data, enables EOS determinations and corresponding semi-empirical evaluations of > 2000 °C thermodynamic states including energy release from bororganic formulations. Our thermochemical model propitiously predicts boronated hydrocarbon shock Hugoniot results.

KEYWORDS HBO₂, Speed of Sound, High Pressure Equation of State, Photoacoustic Light Scattering, Chapman-Jouguet, Thermochemical, Exponential-6, Double-slit experiment
Fluid state high-pressure and temperature physiochemical processes involving metallic and carbon containing reactants are ubiquitous in nature and command the interests of an extraordinary range of interdisciplinary and technological endeavors e.g., astro- planetary- geo- and atmospheric sciences, nuclear engineering, combustion and high explosive materials science, and explosive crystallization of technologically important materials to name but just a few.\textsuperscript{1-7} Quantitative predictions of extreme-condition chemistry are inexorably linked to knowing EOS of probable major reaction species. For example, the optimal use of metal fuel additives to enhance the release of chemical energy stored in organic crystals has been stymied by the lack of oxide component EOS data. Aluminum (Al) powder has long been proposed as a promising candidate fuel to significantly increase chemical power output of highly energetic (HE) material formulations.\textsuperscript{8} Large-scale tests revealed that Al additives actually decrease shock pressure and reaction velocities of HEs, an effect later attributed to low heat of formation oxide products at the Chapman-Jouguet (C-J) state of explosives, i.e. the thermodynamic state where reaction products behind a steady propagating detonation front reach chemical equilibrium.\textsuperscript{6} It is now well understood that exothermic reactions must meet or exceed high melt temperatures of metal oxides before fuel enhancement can be achieved. Inability to realize the full potential of Al fuel lead to consideration of utilizing boron, which has the highest elemental heat of combustion $\Delta H = 137.45$ kJ/cc, per unit volume.\textsuperscript{9} Combustion enhancement using boron has also proved difficult to harness; the complete oxidation of boron can be poisoned by the presence of a common reaction product, water vapor.\textsuperscript{10} To sufficiently elucidate the chemical energy landscape of metalized propellants or HEs the efficacy of controlled parameters, e.g., metal powder grain size and concentration, pure metal powder vs. metal fractionated compounds, oxidizer and fluorinator concentration, etc. continue to be examined using combustion or large-scale tests. Macroscopic-scale performance metrics e.g., energy release and reaction rate, of tested formulations provides necessary information required to challenge predictions made using EOS based thermochemical models. Thus stringently refined semi-empirical computational models serve to guide and reduce time consuming and dangerous investigations of new formulations.
The study of combustion reactions involving boron has lead to the conclusion that a simple molecular product HBO₂, affects to a significant degree the energy output since it is an effective molecular trap to boron on its path to full oxidation.¹¹ We hypothesize that HBO₂ will likely have a similar effect on the properties of boron containing HEs. Despite decades of study however there are no EOS type data available of HBO₂ to test such predictions. We present in this paper the first such experimental results on the SoS of HBO₂ at elevated pressures and temperatures. Normally we apply the impulsive stimulated light scattering (ISLS) technique to generate and probe acoustic wave propagation in fluid samples encapsulated within resistively heated diamond-anvil cells (DAC).¹²⁻¹⁴ However there are practical limitations to the ISLS technique applied to optically thin, e.g., <50 µm fluids, 1) they must absorb minimally some of excitation-pulse light and, 2) exhibit no photo reactions with either excitation- or probe-pulses. Unfortunately HBO₂(l) does not absorb the fundamental or higher harmonics of our 1064 nm excitation source. Furthermore we observe a high propensity for HBO₂ photochemistry induced by exposure to overlapped ISLS excitation pulses (1.0-1.4 GW/cm² peak Gaussian profile irradiance) –these issues are common to most fluids over a wide range of available visible to near-IR laser wavelengths.

In this report we introduce a time-domain (T-D) photoacoustic light scattering (PALS) technique to enable in situ SoS measurements from optically thin materials encapsulated under non ambient pressure-temperature conditions. The accuracy of PALS is first established by comparison of H₂O(l) and H₂O(s) SoS measurements with literature results and, in turn, HBO₂(l) results are given to establish an EOS. Advantages of PALS over Brillouin or ISLS approaches are (i) low average irradiance, (1-3 orders of magnitude less than CW laser Brillouin measurements) and low peak irradiance (1-2 orders of magnitude less than pulsed laser transient grating measurements), which significantly reduces the potential for photochemical initiated reactions (ii) inherently low frequency measurements, which helps to avoid or minimize liquid-state acoustic dispersion affects, (iii) at least one order of magnitude in tunable frequency range is available to conduct acoustic dispersion studies that can be very rapidly conducted on glasses and polymers to reveal structural relaxation rates without need to alter incoming
beam angles, wavelengths or the sample position, (iv) optically thin e.g., 5 µm materials can easily be studied with no requirement to absorb excitation- or probe-pulse wavelengths. The technical advantages of using T-D SoS techniques for the study of fluids have been previously discussed. Here we provide SoS data from a material that is highly susceptible to laser-induced photochemistry using an experimental approach that is highly versatile and straightforward to execute.

A PALS transducer is made by depositing a platinum film onto the culet of a diamond-anvil. Focused ion beam (FIB) site-specific deposition is conducted using a FEI Nova600i NanoLab instrument. A culet is first cleaned and then coated with 150-200 Å of carbon to minimize FIB charging effects. A precursor gas, trimethyl platinum (TMP) is introduced approximately 200 µm above a culet surface. TMP interacts with a scanning ion beam whereby Pt deposition ensues at the culet surface. We initially found that four parallel Pt transducers, (0.5-1.0 µm wide, approximately 75 µm long, and 0.27-µm tall), with center-to-center line separations of 22, 25, 30, and 33 µm enable one to measure speeds of sound with velocities ranging from 0.5 to at least 5 km/sec (Figure 1a, 1b). Welding micron dimensional wire onto one anvil by method of compression with an opposing anvil may also work to form a transducer.

To generate sound, a 100 ps optical pulse is focused onto a transducer. The peak laser irradiance, <0.03 GW/cm², impulsively increases temperature in the transducer (electron-phonon energy transfer) by a few degrees. The temperature rise produces a thermal stress distribution in the Pt film that launches a longitudinal strain-pulse. The pulse energy is reflected and transmitted at the interface between the film and the surrounding sample. Transmitted broadband pulses that travel perpendicular to the direction of the excitation-pulse and into the surrounding medium are utilized to make SoS measurements. The physics behind similar photoacoustic transducers is well documented however the geometry and application of our device is unique. At 277 °C and 0.01GPa, the acoustic impedance of Pt ≈ 8.8.0x10⁷ Kg/s·m² and HBO₂(l) = 6.5x10⁷ Kg/s·m² and so the transmitted acoustic intensity Iᵣ of that initially within the film is 2.9%; generally Iᵣ increases with applied pressure because fluids are more compressible than metal, e.g., Iᵣ ≈ 4.2% at 0.5 GPa. The traveling acoustic peak (expansion of the
medium) increases and the acoustic trench (rarefaction following expansion of the medium) reduces the nominal index of refraction of the sample and therefore alters the local magnitude of optical diffraction. A time-of-flight delayed 532 nm probe-pulse (~ 20 µm FWHM spot) is focused onto a second and parallel Pt film. Each T-D datum represents the average of at least 800 laser shots and each time series is 500-800 points in length. (In principle, a CW laser probe and a sufficiently fast GHz range detector and oscilloscope could be employed to collect an entire T-D series in real-time.) Probe radiation scatters off of the Pt films forming a local oscillator (LO) or reference field, \( E_R, (I_R= E_R^2) \) with a constant phase. Probe radiation also diffracts from the traveling wave, generating a diffracted field, \( E_D, (I_D= E_D^2) \) with a time-varying phase. A pin-hole aperture is positioned behind the DAC to select a signal collection wave-vector, \( K_s \) and pass a narrow cone of light (<1x10^-4 % of the available DAC solid angle) to a photomultiplier tube, (PMT). Signal intensity measured at the PMT is equal to the square of the mixed (heterodyne detection) fields, and is modulated by the time varying optical phase difference between \( E_R \) and \( E_D \). Here the frequency of the material response is given by \( \nu_A = 2c/\lambda_p (\sin \theta/2) \), where \( c \) is the adiabatic SoS, \( \lambda_p \) is the probe wavelength, and \( \theta = \theta_{pi} + \theta_{pd} \), the probe angle of incidence and the probe angle of diffraction. The phenomenon described here is analogous to Thomas Young’s well-known double-slit diffraction experiment where here the slit separation, i.e. the distance between the traveling wave and the point where \( I_R \) is generated, is time dependant. Time-domain series (Fig. 2a) are Fourier transformed to compute modulation frequency (\( \nu_A < 2 \) GHz for \( \theta = 10^\circ, c \leq 6 \) km/sec, \( \lambda_p = 532 \) nm.). A Web-enhanced object, an animation, of the PALS process is available in Quicktime format.

The selected value of \( K_s \) is determined by conducting PALS measurements from water where accurately established \( c(P,T) \) data are published. PALS measurements compare favorably to the well-established IAPWS-95 formulations (standard deviation is 0.6%) including accurate ISLS results (Figure 2b). A powerful feature of PALS allows for a continuum of \( K_s \) values to be accessed for rapid investigations of dispersion relations without need to physically change \( \theta_{pi} \) or the sample position (\( \nu_A = 0.4 – 4.0 \) GHz for \( \theta = 5^\circ - 53^\circ, c = 2.4 \) km/sec, and \( \lambda_p = 0.532 \) µm). High P-T SoS are determined
by, $c = \nu / K_s$. Recent improvements, e.g., the use of a cylindrical probe profile, have reduced the error to <0.5%.

The molecular stability of HBO$_2$ was verified by µ-FTIR up to 277 °C and 0.7 GPa. At 277 °C HBO$_2$ begins to slowly freeze above 0.22 GPa. In this pressure range the interpolated melting curve is relatively steep, 490 °C/GPa. Above 300-350 °C, fluorescent optical manometers consistently failed within 60 minutes; perhaps the oxidation potential of the fluid increased. The narrow P-T region where precise fluid-state HBO$_2$ measurements are accessible may explain the lack of any previous data. SoS results for HBO$_2$(l) are plotted in Fig. 3.

The SoS data provide an opportunity for deriving effective intermolecular interactions for the HBO$_2$ product, thus enabling accurate predictions of thermodynamic and chemical equilibrium states of highly energetic reactions involving boron containing or loaded compounds. To this end we employ an EXP6-polar thermodynamics theory that was previously shown to yield very good results for the properties of hot, dense water as well as those of HNO$_2$. HBO$_2$ is also a strongly polar molecule, with a dipole moment larger than H$_2$O; for the purpose of modeling HBO$_2$ we set the value of its dipole moment to the calculated value for the isolated molecule, $\mu = 2.78$ Debye. It is possible and quite likely that, similarly with H$_2$O, a somewhat larger value of $\mu$ may be more appropriate for describing HBO$_2$ at the high density fluid conditions typical of detonation or high pressure combustion, whose properties we eventually wish to predict. However, the limited experimental data presently available do not warrant trying to discern such an effect; we expect that this approximation will have little effect on our conclusions regarding the character of detonations containing boron, which at this point can only be largely qualitative. We find that EXP6 parameter values, $r_\sigma = 3.976$ Å, $\varepsilon = 216.3$ K, and $\alpha = 12.67$ using the above dipole moment yield good agreement with the SoS measurements - see Figure 3. Thermodynamic calculations using these parameters place the critical point of HBO$_2$ approximately at $T_c = 447$ °C and $P_c = 260$ atm; of course chemical reactivity may actually intervene before these conditions can be reached.
The important role that molecular HBO₂ is likely to play in hydrocarbon or organometallic explosive combustion of boron particles (e.g. in rocket propellants and ramjet fuels) is well documented.

Here we attempt to quantify its impact in the detonation of explosives containing elemental boron by employing the newly determined HBO₂ thermodynamics in the calculation of detonation velocities. These calculations are performed using the code CHEETAH and are similar with those described for example in Ref. 31. The code is used here to determine C-J points of explosives. Detonation product results are constrained to single-phase fluid mixtures and, potentially, many condensed phases. The major boron-containing products likely to be relevant for such processes have been discussed for example by Akimov et al..

The fluid phase components we consider are small molecular products such as N₂, CO₂, H₂O, CO, NH₃, CH₄, HBO₂, O₂, H₂, etc., which are thermodynamically favored at high temperatures and pressures; they are all modeled by EXP6 or EXP6-polar interactions and tested favorably against experimental data. The condensed phases are carbon (diamond and graphite), B₂O₃ (liquid and solid), B (solid and liquid), BN (cubic and hexagonal solids), CB₄ (solid) and H₃BO₃ (solid), all described by Murnaghan-type EOS. Among these B₂O₃ is of particular importance; it is likely the oxidation end-point of boron. Unfortunately B₂O₃ experimental data are very scarce. We note however that our liquid EOS is in good agreement with the simulation results of Ohmura et al., and the melting line agrees well with that reported by Brazhkin et al. (Figure. 4a).

Nevertheless, such uncertainties due to the lack of EOS data for likely major reaction products, probably limit our ability to make fully quantitative predictions.

The combustion of solid boron particles is plagued by well known kinetics issues, which are likely to also be important in the detonation of explosives loaded with metallic boron, just as in the case of aluminum-loaded compositions. We attempt to circumvent these complications and focus therefore on explosive mixtures with boronated organic compounds, which were studied experimentally. These are, 1) 86% (by weight) pentaerythritol tetranitrate (C₅H₈N₄O₁₂) + 14% orthocarborane (C₂B₆H₁₂), 2) 75% tetryanitromethane (CN₄O₈) + 25% pentaborane (B₅H₉), and 3) 70% tetryanitromethane + 30% borazine (B₃N₃H₆); their initial densities are ρₒ = 0.78, 1.14, and 1.28 g/cc, respectively. The experimental
detonation velocities reported are $D_{\text{exp}}=4.64$, 5.9, and 6.3 km/s; our corresponding calculated values are $D_{\text{calc}} = 4.78$ ($\Delta=3.02\%$), 5.96 ($\Delta=1.02\%$) and 6.13 ($\Delta=-2.70\%$) km/s, respectively, indicating reasonable agreement. For these energetic mixtures we find that the major detonation products containing boron are HBO$_2$ and B$_2$O$_3$(l) (mixture two also yields a small amount of liquid boron), mixed with the molecular detonation products typical for CHNO explosives. We show for example in Figure 4b the C-J region composition of mixture 3), which indicates, as expected, that large amounts of water also result upon detonation. Since the reaction of B$_2$O$_3$ (l) with water is likely an important route toward the formation of HBO$_2$, its study at high temperatures and pressures will significantly increase the confidence of quantitative predictions of the thermodynamic and kinetic behavior of boron containing explosives and propellants.$^{10}$

Our study reveals that the reaction of B$_2$O$_3$ (l) + H$_2$O(v) is a plausible route toward the formation of HBO$_2$ under detonation conditions. Previously the collection of accurate SoS data using in situ measurement techniques was hindered by materials that exhibit high photosensitivity and/or limited P-T regions of chemical stability. SoS data from HBO$_2$(l), suggest, that we can utilize EOS based thermochemical models to predict high-pressure combustion, deflagration, and detonation chemistry involving boron: a reasonable level of confidence for computing metal assisted high-energy reactions has been achieved. We also make note that in situations where a carbon deficient oxidizer e.g., ammonium perchlorate (NH$_4$ClO$_4$), reacts with 10 % wt. boron, our calculations predict up to five times more HBO$_2$ product is likely to be found compared to results given above –an expected result given that the concentration of oxygen competing carbon products, e.g. CO, CO$_2$, is severely diminished. We expect that the relative simplicity and high versatility of PALS type measurements will assist research initiatives directed to understand a wide-array of extreme condition chemical processes.
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Figure 1. (a) A TEM image of platinum films deposited onto a diamond-anvil. (b) A photo-micrograph of a DAC sample chamber. At 0.4 GPa and 277 °C solid HBO₂ slowly encroaches on the supercooled fluid. Inspection of the left side of the chamber reveals gratings that were burned into the culet from failed attempts to generate traditional ISLS signals. A pressure manometer rests in the lower left region of the chamber.
Figure 2. (a) PALS time-domain signals from liquid H$_2$O and HBO$_2$. (b) Determination of $K_S$ is accomplished by measuring $\nu_A$ from a sample of known $c(P,T)$. $K_S$ was selected using the IAPWS-95 value for H$_2$O SoS at 0.66 GPa and 22 °C; PALS results compare well with liquid and solid state measurements of Abramson and Baer.\textsuperscript{14,21,22}

Figure 3. Measured SoS from HBO$_2$(l), filled circles, and calculated SoS from EXP6-polar function, solid line.
Figure 4. (a) Calculated $\text{B}_2\text{O}_3$ melt curve from CHEETAH (solid line) compared to experimental data (open squares) from Brazhkin et al..\(^3\) (b) Calculated C-J plane decomposition mixture from 70% tetranitromethane + 30% borazine ($\text{B}_3\text{N}_3\text{H}_6$).

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SYNOPSIS TOC We introduce a highly versatile and straightforward photoacoustic light scattering technique, (PALS) which enables direct time-domain speeds of sound measurements of fluids and solids encapsulated under extreme pressure-temperature condition. The process begins when an acoustic wave is photoelastically launched from a metal transducer. A time-of-flight delayed cylindrical probe beam scatters off the transducer and a traveling wave. These two diffracted fields mix in an analogous way to Thomas Young’s double-slit experiment, except here one slit travels at the SoS of the sample medium. The optical field emission (wave interference) provides a continuum of measurable ultrasonic frequencies. Aperture selection of a small scattering wavevector range enables collection of signal with sufficient phase coherence to determine the SoS with > 99.5 % accuracy. Here we employ PALS to study a fluid boron oxide within a heated diamond-anvil cell in order to develop and stringently test equation of state based thermochemical predictions.