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1 **Speed of sound measurements in deuterium oxide (D<sub>2</sub>O) at temperatures between**  
2 **(276.97 and 363.15) K and at pressures up to 210 MPa**

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6 This paper presents speed of sound measurements in heavy water (deuterium ox-  
7 ide, D<sub>2</sub>O) along six isotherms **between 276.97 K and 363.15 K** for pressures up to  
8 210 MPa **using a** double *pulse-echo* method. The experimental **apparatus** was **val-**  
9 **idated measuring the speed of sound in** ordinary water at ambient pressure and at  
10 temperatures between 295.5 K and 363.15 K **with results found in** agreement with  
11 values calculated from the reference equation of state for water by Wagner and Pruß  
12 **within** 0.005 %. The relative combined expanded uncertainty **of our** speed of sound  
13 measurements, at a confidence level of 95 %, is estimated to be less than 0.03 % for  
14 pressures up to 10 MPa and in the order of 0.05 % for pressures up to 210 MPa in the  
15 whole investigated temperature range. The speed of sound results have been com-  
16 pared with values calculated from the reference equation for heavy water the IAPS84  
17 Formulation by Hill et al. (1982), and with **the prediction of the** newly developed  
18 equation of state for heavy water by Herrig *et al.* (2018). The relative deviations  
19 **of these comparison were found to be consistent with the reference equations within**  
20 **their combined uncertainty.** The **results presented here were also compared** with the  
21 most recent data by Wegge *et al.* **and found to be in agreement within** 0.05 %.

22 **Keywords:** Speed of sound, deuterium oxide, heavy water, high pressure

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## 23 I. INTRODUCTION

24 Liquid deuterium oxide (often referred to as heavy water) is of interest in various scientific  
25 fields for its numerous applications, e.g. to study mechanisms and rates of chemical or nuclear  
26 reactions, for diagnostics in nuclear magnetic resonance, as well as in biological processes  
27 and as coolant and moderator in pressurized heavy-water reactor (PHWR) of nuclear power  
28 plants. A dedicated equation of state (EoS) is a useful tool to represent the ensemble of  
29 thermodynamic properties needed to develop novel technological and industrial solutions.  
30 The dedicated EoS of a fluid can reach high accuracy when also caloric properties (such as  
31 speed of sound and specific heat capacity) are included in its implementation. High pressure  
32 speed of sound measurements are of special interest because, being linked to both calorific  
33 and mechanical properties of the fluid, they drive the choice of the number of terms that  
34 are included in the equation of state and allow to improve its accuracy, and the physical  
35 behaviour. Differently from the case of water, the thermodynamic properties of heavy water  
36 are far less studied and measurements are usually affected by a larger uncertainty. The  
37 measurement accuracy significantly improves for atmospheric pressure measurements and  
38 a complete list of references of these measurements is reported in Table 13 of Herrig *et*  
39 *al.*<sup>1</sup> Anyway, since in this work the minimum pressure has been limited to 0.2 MPa (for  
40 preventing the possible contamination of the fluid), a direct comparison with the results  
41 reported at 0.1 MPa is not possible, unless by extrapolation.

42 Considering high pressure speed of sound measurements the availability of published  
43 papers reduces to few works. In this case, mention is worth for the speed of sound results  
44 obtained by Wilson<sup>2</sup> or by Chen and Millero<sup>3</sup> up to 100 MPa, those obtained by Aleksandrov  
45 and Larkin<sup>4</sup>, and the very accurate values by Wegge, Richter and Span (2016)<sup>5</sup>. Some of  
46 these data have been used by Hill *et al.*<sup>6</sup> to implement a fundamental equation of state, any-  
47 way that equation has a limited range of validity with a lower limit temperature of 276.97 K  
48 and a maximum pressure of 100 MPa. More recently, a more accurate reference equation  
49 of state has been implemented by Herrig *et al.*<sup>1</sup>, but a definitive uncertainty estimation for  
50 pressures above 100 MPa is not possible, because speed of sound data were not available in  
51 this high pressure region. Motivated by this limited framework, we carried out more than  
52 seventy experimental speed of sound measurements in heavy water (deuterium oxide, D<sub>2</sub>O;  
53 purity: 99.85 % D atoms, deuterium atoms fraction), as reported and discussed in the rest

54 of this work. Our experimental results have been obtained along six isotherms ranging from  
55 (276.97 to 363.15) K and for pressure up to 210 MPa. The results presented here are the  
56 only data available in this range of pressure, making them useful to improve and update a  
57 new dedicated equation of state<sup>1</sup> or, at least, they contribute to validate the equation and  
58 provide an estimation of its accuracy when thermodynamic properties are extrapolated.

## 59 II. EXPERIMENTAL SECTION

60 Speed of sound was measured by a double *pulse-echo* ultrasonic technique. The core  
61 of the experimental apparatus, used for the determination of the phase velocity of the  
62 ultrasonic waves, is a cylindrical stainless steel cell supplied with two reflectors placed at  
63 unequal distances from a single piezoelectric transducer. The main features of the apparatus  
64 design (with regard to the dimensions, constructing materials, gaskets, and because of the  
65 absence of moving parts) make it a versatile instrument **which can be operated** over a wide  
66 range of temperatures and pressures. The double *pulse-echo* method is based on direct  
67 measurement of the **time delay** between echoes coming from the different reflectors. In a  
68 previous paper<sup>7</sup>, details about the ultrasonic cell and the associated experimental apparatus  
69 are provided. The adopted measurement design allows to compensate the effects due to  
70 the trigger and electrical line delays but, even more **importantly**, this configuration allows  
71 to obtain a repeatability of the time-of-flight measurements in the order of 10 parts per  
72 million since **tone bursts** have very similar shapes. In figure 1, a geometrical **sketch** of  
73 the measurement cell is shown. The nominal lengths of the spacers, separating the source  
74 (red) from the reflectors are  $L_1 = 45$  mm and  $L_2 = 67.5$  mm. The acoustic path length **was**  
75 **estimated by the results of a calibration based on speed of sound measurements in** high-purity  
76 ordinary water (H<sub>2</sub>O) at seven different temperatures (295.5, 303.15, 304.0, 319.0, 323.15,  
77 343.15, 363.15) K and ambient pressure, with reference speed of sound values obtained from  
78 the IAPWS-95 formulation<sup>8</sup>.

79 Additional **experimental** tests have been carried out to verify that calibrated  $\Delta L$  ( $\Delta L =$   
80  $L_2 - L_1$ ) **did not vary, depending on the** carrier frequency adopted to generate the signal.  
81 Three different runs have been performed using tone-burst of 5 cycles with a carrier frequency  
82 of 4 MHz and three **additional** runs with a carrier frequency of 8 MHz. Since the frequency  
83 dependence of the time-of-flight **has been verified to be** negligible, when compared to other

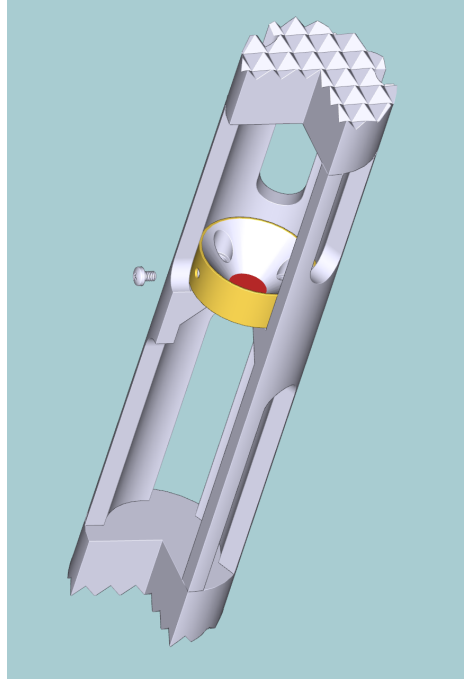


Figure 1. Layout of the ultrasonic measuring sensor<sup>10</sup>.

$p = 0.1$ MPa	$2\Delta L$ / mm	$2\Delta L$ / mm	Relative	$2\Delta L$ / mm
$T = 294.95$ K	Calibration 1	Calibration 2	deviations	Mean value
	(3 runs)	(3 runs)		
$f = 4$ MHz	43.8029	43.8017	0.0026 %	43.8023
$f = 8$ MHz	43.8047	43.8037	0.0022 %	43.8042
Relative deviation				0.0043 %

Table I. Results of the cell calibration procedure obtained using different carrier frequencies.

84 sources of uncertainty, the speed of sound measurements were eventually performed at  
 85 4 MHz. To minimize the effect of temperature drifts in the order of a few millikelvin, the  
 86 calibration has been repeated three times and the results have been averaged. All these  
 87 preliminary tests were carried out at ambient pressure and  $T = 294.95$  K. The results have  
 88 been summarized in Table II. In figure 2 the overlapping of the two echoes (black and gray)  
 89 obtained at 4 MHz (a) and at 8 MHz (b) are shown.

90 The relative deviations of our experimental results ( $w_{\text{INRiM}}$ ) from  $w_{\text{EoS}}$ , such as the speed  
 91 of sound values calculated with the equation of state (EoS) of Wagner and Pruf<sup>8</sup>, are  
 92 plotted as a function of the temperature in figure 3. The uncertainty declared by Wagner

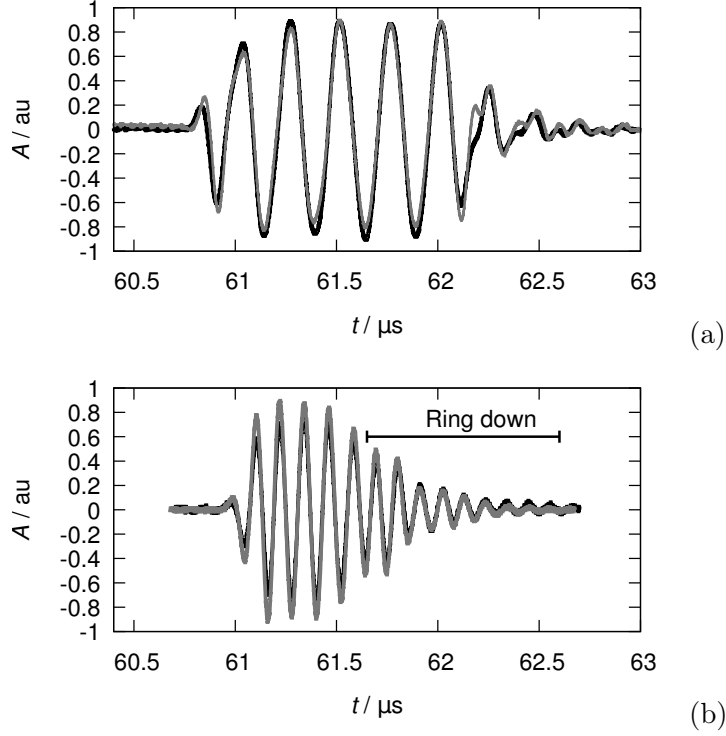


Figure 2. Plots of the five-cycles tone-bursts obtained with a 4 MHz carrier frequency (a) and 8 MHz (b) using a wide-band piezoelectric source with nominal resonant frequency of 8 MHz.

93 and Pruß for the [speed of sound predicted by equation](#), in the specific considered region, is  
 94 only 0.005 %. [Remarkably, all our experimental results](#) are in a good agreement with the  
 95 reference equation of state.

96 The piezoelectric transducer [is excited](#) with an electrical signal [from a function generator](#)  
 97 in the form of five-cycles repeated tone-bursts with a carrier frequency of 4 MHz and an am-  
 98 plitude of 10 Vpp. The waveforms, including both echoes, have a duration of approximately  
 99 100  $\mu s$  and are digitized at a sampling rate of  $4 \times 10^9$  samples per second. [By analyzing](#)  
 100 [the sampled signals, the time-of-flight  \$\tau\_{exp}\$  of the ultrasonic waves that travelled twice the](#)  
 101 [distance separating the source and reflectors is determined.](#) The speed of sound,  $w_{exp}$ , is  
 102 [then](#) obtained from the following expression:

$$w_{exp} = \frac{2\Delta L}{\tau_{exp}}, \quad (1)$$

103 where  $\Delta L$  is the difference in the acoustic paths travelled by the first two echoes coming from  
 104 different reflectors and  $\tau_{exp}$  is the corresponding time delay. The time delay is determined  
 105 on the basis of the digital signal  $P_1(t)$ , representing the first sampled echo from the nearest

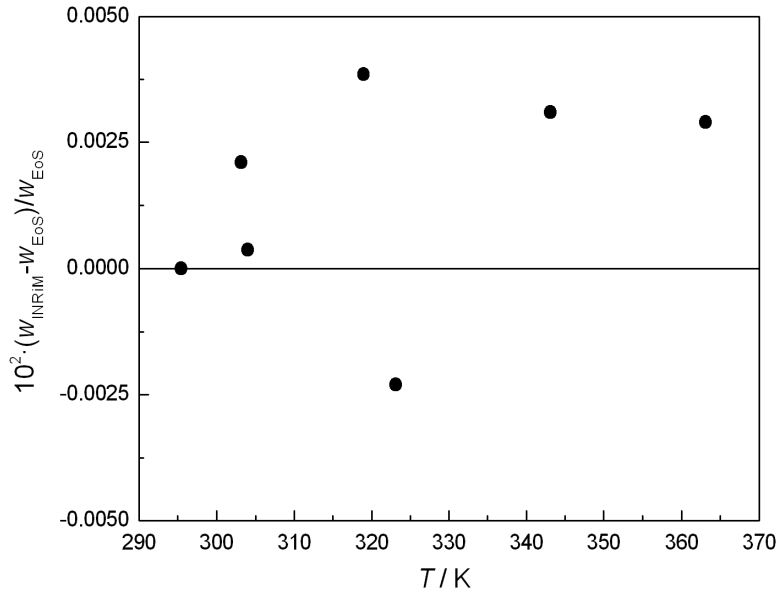


Figure 3. Results of the calibration of the speed of sound sensor in ordinary (light) water at  $p = 0.098$  MPa. Relative deviations of experimental speeds of sound  $w_{\text{INRiM}}$  from values  $w_{\text{EoS}}$  calculated with the EoS of Wagner and Pruß<sup>8</sup> are plotted as a function of the temperature  $T$

106 reflector, and the echo  $P_2(t + \tau)$ , from the farthest reflector, by means of a correlation  
 107 function  $C(\tau)$  defined as:

$$C(\tau) = \int_{-\infty}^{\infty} P_1(t)P_2(t + \tau)dt, \quad (2)$$

108 that has the property to show an absolute maximum at the value of  $\tau$  equal to the time delay  
 109 between the two echo waveforms. A detailed explanation of this method and the associated  
 110 signal-to-noise ratio are discussed in Benedetto *et al.*<sup>7</sup>.

111 Experimental measurements of times-of-flight and travelled path-lengths can be used to  
 112 determine the speed of sound after [keeping into account relevant corrections](#). In Lago *et*  
 113 *al.*<sup>9</sup>, it is shown how the finite dimensions of the source prevent the complete cancellation of  
 114 [the phase shift affecting the wave-fronts spreading into the measurement cell](#). The described  
 115 [diffraction effects perturb the measurement of the time-of-flight, which is accounted by](#)  
 116 [correcting the expression used to determine the speed of sound as follows](#):



Figure 4. Wide-band ceramic PZT “DuraAct” kapton encapsulated.

$$w_{\text{exp}} = \frac{2\Delta L}{\tau_{\text{exp}} + \delta\tau}, \quad (3)$$

117 where the correction term  $\delta\tau$  comes from the wave-like nature of the spreading signal. The  
 118 diffraction of the generated signal appears in the form of a phase advance of the ultrasonic  
 119 pulses, relative to a perfectly plane wave traversing the same distance with resulting effects  
 120 on  $\delta\tau$  which can be calculated using an appropriate model<sup>9</sup>.

121 For speeds of sound, measured at temperature  $T$  and pressure  $p$  which differ from the  
 122 calibration conditions  $(p_0, T_0)$ , the acoustic paths  $L_1$  and  $L_2$ , and their difference  $\Delta L$ , have  
 123 to be corrected using the thermal expansion coefficient  $\alpha$  and compressibility coefficient  $\beta$   
 124 of the AISI-316L (namely the material comprising the measuring cell), according to the  
 125 following relation:

$$\Delta L(p, T) = \Delta L(p_0, T_0) [1 + \alpha(T - T_0) - \beta/3(p - p_0)]. \quad (4)$$

126 The wide-band ceramic PZT “DuraAct” kapton encapsulated, shown in figure 4 and used  
 127 both as the source and the receiver of the acoustic signals, has a diameter of about 10 mm  
 128 and is clamped by conical reflectors that reduce its effective radius to about 7 mm without  
 129 changing the thickness of the disc; as a matter of fact, the nominal resonant frequency of  
 130 8 MHz is not perturbed by this type of clamping, as demonstrated by the long ring down  
 131 time shown in figure 2(b).

132 The ultrasonic cell is set in an AISI-316L pressure vessel that can operate in the tempera-  
 133 ture range between (240 and 420) K and for pressures up to 300 MPa, sealed with AISI-316L  
 134 metallic gaskets. Depending on the pressure range, one of three Honeywell pressure trans-  
 135 ducers with full-scale ranges of (10, 50, and 300) MPa was used, while the temperature is



136 measured by means of two PT100 thermometers inserted in the top and the bottom ends of  
137 the pressure vessel. These thermometers were calibrated in the range of (230 and 390) K by  
138 comparison with INRiM's (Istituto Nazionale di Ricerca Metrologica) Standard Platinum  
139 Resistance Thermometer (SPRT) directly traceable to the National Temperature Standard.

140 A liquid bath thermostat maintains the temperature of experiment with a long term  
141 stability better than  $\pm 1$  mK, over the whole working range, and is composed by a primary  
142 external thermostat that can reach a stability of 10 mK and a secondary Proportional  
143 Integrative and Derivative control (PID), providing feedback to achieve a finer temperature  
144 control.

#### 145 A. Preparation of the apparatus

146 Speed of sound measurements along six isotherms at temperatures of (276.97, 283.15,  
147 303.15, 323.15, 343.15, 363.15) K have been carried out. For each isotherm, measurements  
148 were taken starting at the pressure of 210 MPa and decreasing the pressure down to low  
149 pressure. The high pressure control system has been initially cleaned using volatile solvents  
150 and evacuated. Then, the entire high pressure manifold was rinsed with heavy water and  
151 subsequently drained and dried by a flow of compressed dry nitrogen several times. The  
152 system was then evacuated for 24 h by a trapped mechanical pump, to eliminate any residual  
153 trace of fluid and/or air. In order to prevent the possible contamination of the sample and  
154 the influence of dissolved gases, the pressure vessel, containing the ultrasonic cell, was filled  
155 under vacuum, by extraction of pure deuterium oxide from an ambient pressure reservoir.  
156 Successively, the system was filled at the maximum planned pressure, with the purpose of  
157 tensioning the main seal of the pressure vessel, while it was immersed in the thermostatic  
158 bath. After loading the measuring system with the sample, it was necessary to wait about 8 h  
159 to ensure that thermodynamic equilibrium has been reached. Pressure decrements along one  
160 isotherm were carried out slowly, taking care not to exceed a decrease rate of 0.1 MPa/s, to  
161 preserve the validity of the calibration of the pressure transducers. Following each successive  
162 pressure decrease, a temporary cooling of the liquid in the cell of about 10 mK was observed.  
163 This temperature change was recovered, by the action of the thermostatic bath, in about  
164 one hour. The completion of this transitory phase was observed by continuous monitoring  
165 the time-of-flight within the ultrasonic cell and by the temperature readings of the two

<b>Product name:</b>	Deuterium Oxide, 99.9 % D atoms	<b>Molecular Formula:</b>	D <sub>2</sub> O
<b>Molecular Weight:</b>	20.03	<b>Assay (Quantitative NMR):</b>	99.90 % D atoms
<b>Appearance (color):</b>	colourless	<b>Appearance (form)</b>	Liquid

Table II. Specification of the used sample as reported by the certificate of analysis.

166 thermometers. When measurements on an isotherm were completed, changes of about 10 K  
167 were brought to the system in preparation for the next isotherm. In optimal conditions, the  
168 thermodynamic equilibrium could be recovered after approximately 12 h.

169 The sample of deuterium oxide (D<sub>2</sub>O) was supplied by Sigma-Aldrich. The declared spe-  
170 cific mole fraction purity of this sample was better than 99.9 % D atoms. No further analysis  
171 or purification was attempted. Some cautions have been taken to try to preserve the purity of  
172 the sample. For example, to limit the contamination due to air humidity, bottles have been  
173 opened in a climatic room with relative humidity, at ambient temperature, below 20 % and  
174 sealed with a valve immediately afterwards. Specification of the used D<sub>2</sub>O sample has been  
175 reported in table II, as declared by the supplier. Despite taken precautions, density changes  
176 have been observed when the sample has been analyzed after speed of sound measurements  
177 had been carried out. For this reason, the speed of sound results have been associated to a  
178 composition in between the two compositions (99.85 % D atoms) and a further contribution  
179 to the uncertainty budget has been added for accounting of the uncertainty of the sample  
180 composition.

### 181 III. SPEED OF SOUND RESULTS AND COMPARISON WITH 182 EQUATION OF STATE PREDICTIONS

183 Speed of sound measurements in heavy water were carried out in the temperature range  
184 from (276.97 to 363.15) K and pressures up to 210 MPa. The repeatability of the measure-  
185 ments has been checked for the isobar at 100 MPa, resulting in the order of 0.002 %. The  
186 relative combined expanded uncertainty ( $k = 2$ ) for the speed of sound measurements was  
187 estimated to be between 0.03 % and 0.05 %. Since one of the most important contribution to  
188 the speed of sound uncertainty comes from imperfect estimate of the experimental pressure,  
189 the budget has been separately prepared to consider a low pressure range with  $p < 10$  MPa  
190 and a high pressure range with  $10 < p/\text{MPa} < 210$  as reported in table III.

Source of uncertainty	Relative uncertainty	Relative uncertainty
	( $p < 210$ MPa)	( $p < 10$ MPa)
Acoustic path length	0.0065 %	0.006 %
Time-of-flight	0.0010 %	0.001 %
Temperature	0.0070 %	0.007 %
Pressure	0.0197 %	Negligible
Repeatability	0.0020 %	0.002 %
Purity ( 99.85 % D atoms)	0.0070 %	0.007 %
Overall expanded uncertainty ( $k = 2$ )	0.051 %	<0.03 %

Table III. Contributions to the **standard** uncertainty of speed of sound measurements **calculated including the corresponding sensitivity coefficients**.

191 Speed of sound measurements have been carried out along six isotherms. The distribution  
192 of **the experimental pressure along all these isotherms is not the same**. Table IV lists the  
193 **experimental speed of sound** results, while figure 5 and 6 show the corresponding plots, as  
194 a function of **pressure and temperature**, respectively.

$T / \text{K}$	$p / \text{MPa}$	$w_{\text{exp}} / \text{m s}^{-1}$
276.97	0.93	1322.00
276.97	2.03	1323.39
276.97	4.01	1326.00
276.97	10.02	1334.18
276.97	30.00	1363.01
276.96	50.04	1394.37
276.97	70.00	1427.23
276.98	99.94	1478.17
276.98	99.95	1478.35
276.97	130.06	1529.92
276.97	160.05	1580.62
276.97	180.07	1614.23
276.98	199.95	1646.91
276.97	209.97	1663.14
277.15	209.95	1663.78
283.16	0.16	1347.86
283.16	10.03	1361.68
283.16	30.01	1391.17
283.15	50.01	1422.20
283.16	69.98	1454.32
283.16	99.98	1503.65
283.16	130.11	1553.42
283.14	159.99	1602.33
283.13	180.08	1634.58
283.15	200.35	1666.55
283.16	210.39	1682.30
303.15	0.21	1412.35
303.15	10.05	1427.41

$T / \text{K}$	$p / \text{MPa}$	$w_{\text{exp}} / \text{m s}^{-1}$
303.15	30.10	1458.55
303.15	49.98	1489.48
303.15	70.07	1520.73
303.15	100.09	1567.31
303.16	129.92	1612.94
303.15	160.09	1658.46
303.16	180.06	1688.03
303.16	190.72	1703.52
303.15	200.11	1717.13
303.15	209.88	1731.26
323.15	0.24	1447.45
323.15	10.07	1463.63
323.15	29.99	1496.13
323.15	50.05	1528.18
323.15	69.96	1559.43
323.15	100.09	1605.79
323.15	130.02	1650.63
323.15	160.06	1694.30
323.15	180.22	1723.07
323.15	200.07	1750.88
323.15	210.16	1764.70
343.15	0.24	1460.86
343.15	10.15	1478.45
343.13	30.08	1512.94
343.14	30.11	1513.02
343.14	50.01	1546.28
343.15	70.09	1578.75
343.15	100.16	1626.01

$T / \text{K}$	$p / \text{MPa}$	$w_{\text{exp}} / \text{m s}^{-1}$
343.15	129.99	1671.09
343.15	160.08	1714.78
343.15	180.27	1743.34
343.15	200.09	1770.97
343.15	209.75	1784.21
363.15	0.24	1457.29
363.15	10.06	1476.36
363.15	29.98	1513.27
363.15	49.91	1548.69
363.14	70.05	1583.21
363.15	100.05	1632.00
363.14	130.06	1678.67
363.14	160.10	1723.09
363.15	180.16	1751.88
363.15	200.12	1779.84
363.15	209.90	1792.96

Table IV: Speed of sound experimental values ( $w_{\text{exp}}$ ) in D<sub>2</sub>O as a function of the temperature and pressure. The overall expanded relative uncertainty ( $k=2$ ) of the experimental results is  $u(w_{\text{exp}}) = \pm 0.03 \%$  for pressure below 10 MPa and  $u(w_{\text{exp}}) = \pm 0.05 \%$  for pressure above 10 MPa.

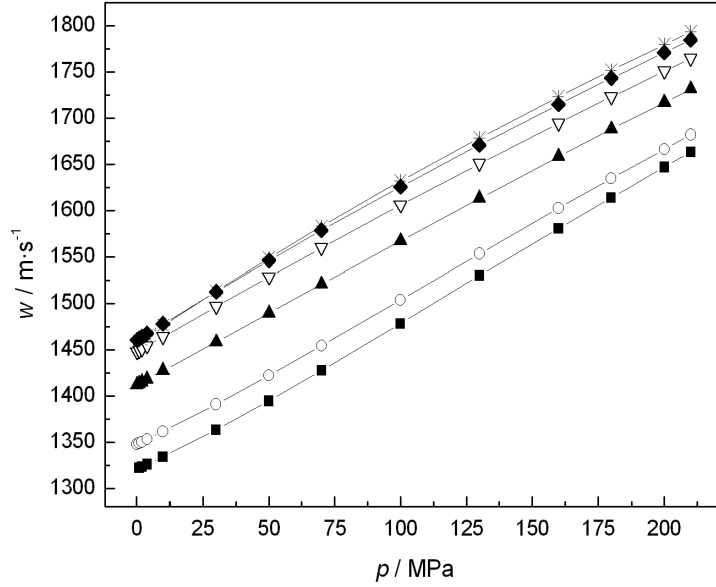


Figure 5. Speed of sound results in deuterium dioxide as a function of pressure. Measurements are affected by an expanded relative uncertainty ( $k = 2$ ) of 0.03 % for pressure up to 10 MPa and 0.05 % at higher pressure. Results are shown by isotherms: (■) 276.97 K; (○) 283.15 K; (▲) 303.15 K; (▽) 323.15 K; (◆) 343.15 K; (\*) 363.15 K.

195 Figure 5 shows intersecting isotherms (343.15 K and 363.15 K); this is expected since  
 196 the pressure derivative of  $w$  significantly varies at low pressure for temperatures higher  
 197 than  $\sim 348$  K. The characteristic shift of the speed of sound maximum value towards higher  
 198 temperatures, for increasing pressure, is show in figure 6. All the measurements along the  
 199 isotherms have been carried out down to a minimum pressure of 0.2 MPa with the exception  
 200 of the one at 276.97 K which was limited to 1 MPa.

201 The experimental results obtained in this work were not used to implement the today  
 202 most updated fundamental equation of state for heavy water (IAPWS-2017) by Herrig *et*  
 203 *al.*<sup>1</sup> and maintained by the International Association for the Properties of Water and Steam.  
 204 Considering that the here obtained speed of sound measurements carried out are independ-  
 205 ent from those formulations, the comparison with IAPWS-2017 predictions and with the  
 206 previous equation by Hill *et al.*<sup>6</sup>, gives an insight into improvements made by updating the  
 207 equation and on whether the most recent can be further improved.

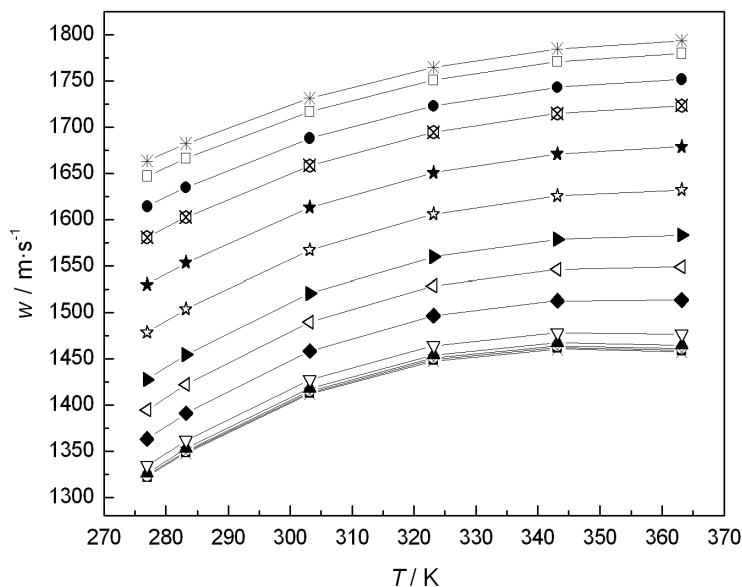


Figure 6. Speed of sound results in deuterium dioxide as a function of temperature. Measurements are affected by an expanded relative uncertainty ( $k = 2$ ) of 0.03 % for pressure up to 10 MPa and 0.05 % at higher pressure. Results are shown by isobars: ( $\times$ ) 0.1 MPa; ( $\blacksquare$ ) 1 MPa; ( $\circ$ ) 2 MPa; ( $\blacktriangle$ ) 4 MPa; ( $\nabla$ ) 10 MPa; ( $\blacklozenge$ ) 30 MPa; ( $\triangleleft$ ) 50 MPa; ( $\blacktriangleright$ ) 70 MPa; ( $\star$ ) 100 MPa; ( $\blackstar$ ) 130 MPa; ( $\otimes$ ) 160 MPa; ( $\bullet$ ) 180 MPa; ( $\square$ ) 200 MPa; ( $*$ ) 210 MPa

208 The relative deviations of our speed of sound from the values calculated with the IAPS84  
 209 formulation of Hill *et al.*<sup>6</sup> and with those calculated with a newly developed equation of  
 210 state for heavy water by Herrig<sup>1</sup> are illustrated in figures 7 and 8, respectively.

211 For temperatures considered in the present work, the latter equation<sup>1</sup> declares 0.015 %  
 212 in the pressure range from (0.1 to 20) MPa, 0.02 % for  $20 < p/\text{MPa} < 50$  and 0.1 % for  
 213  $50 < p/\text{MPa} < 100$ . For pressure above 100 MPa the uncertainty has not been declared since  
 214 speed of sound values were obtained by predictions not validated by experimental results.  
 215 Comparing the plots in figure 7 and 8, it is apparent that the most recent equation<sup>1</sup> performs  
 216 significantly better than the previous one. For example, the maximum relative deviations  
 217 decrease from 1 % to 0.1 % for pressure up to 100 MPa. Furthermore, as reported in figure 9,  
 218 when pressures below 100 MPa are considered, deviations from the equation of state<sup>1</sup> are  
 219 well within 0.07 %.



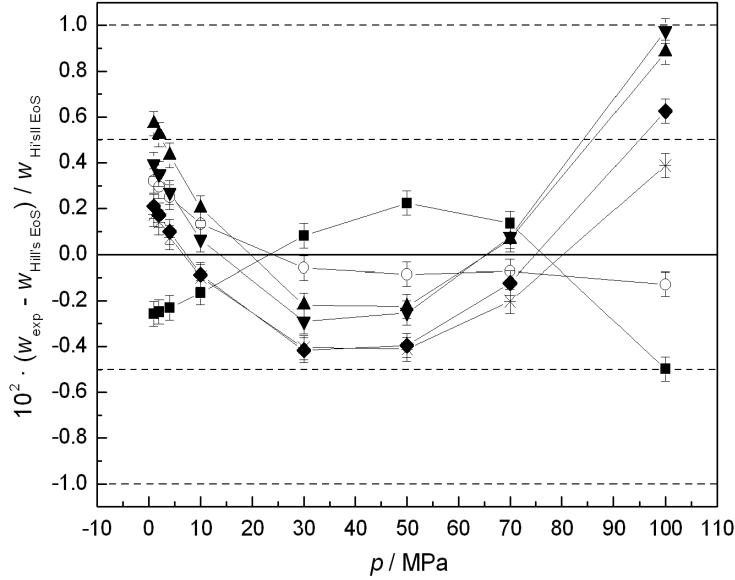


Figure 7. Relative deviation of experimental speed of sound results from Hill's equation of state. This equation has a declared relative uncertainty on speed of sound predictions of 1 % for temperature up to 350 K and 0.5 % above. Symbols correspond to (■) 297.97 K; (○) 283.15 K; (▲) 303.15 K; (▼) 323.15 K; (◆) 343.15 K; (\*) 363.15 K. Reported results are affected by an expanded relative uncertainty ( $k = 2$ ) of 0.03 % for pressure to 10 MPa and 0.05 % at higher pressure.

220 For pressure below 20 MPa, very accurate speed of sound measurements are available from  
 221 Wegge *et al.*<sup>5</sup> with a declared uncertainty of 0.015 %. That experiment was carried out using  
 222 a measurement cell with different lengths of the spacers, a different carrier frequency and a  
 223 different piezoelectric source, both in terms of materials and dimensions, so that obtained  
 224 results can be considered as independent. In Wegge *et al.*<sup>5</sup>, nominal spacers lengths were  
 225 (20 and 30) mm and a 15 mm diameter X-cut quartz crystal was used as an ultrasonic  
 226 source when excited by 30-cycles sinusoidal burst with a carrier frequency of 8 MHz. Quartz  
 227 crystals can operate up to temperature higher than those of ceramic piezoelectric disks  
 228 adopted in this work. Anyway, considering the maximum temperature here investigated,  
 229 both the materials are equivalent. Differences are more evident considering the band-width  
 230 and the sensitivity of the two different sources. Quartz crystals have a lower sensitivity, so

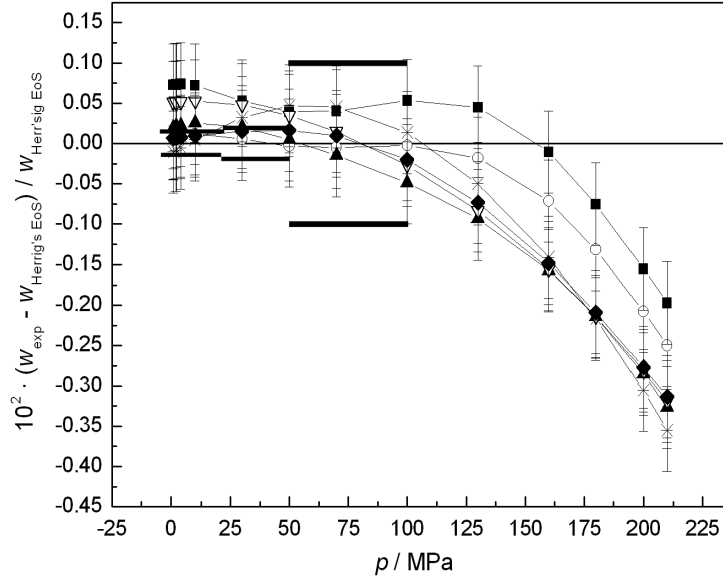


Figure 8. Relative deviation of experimental speed of sound measurements from Herrig's EoS. Reported results are affected by an expanded relative uncertainty ( $k = 2$ ) of 0.03 % for pressure up to 10 MPa and 0.05 % at higher pressure. Symbols correspond to (■) 297.97 K; (○) 283.15 K; (▲) 303.15 K; (▽) 323.15 K; (◆) 343.15 K; (\*) 363.15 K.

231 they need to be excited by a higher number of cycles (30 in that case), before reaching their  
 232 maximum oscillation amplitude. Here adopted wide-band encapsulated ceramic disk can  
 233 reach maximum amplitude oscillation after just three cycles. The quartz crystal intrinsic  
 234 narrow band has the side effect of generating much more oscillations with respect to those  
 235 used to excite the source. For wide-band sources, working out of their resonant frequency,  
 236 only a couple of extra cycles are recorded by the digital oscilloscope. Considering the frame  
 237 of the measurements reported in this work, both the sources perform at the same level since  
 238 in both cases the time-of-flight is measured with a relative uncertainty below 20 part per  
 239 million. The better accuracy obtained by Wegge *et al.* comes from a better measurement  
 240 of the temperature and the pressure, since they have used a Standard Platinum Resistance  
 241 Thermometers and a pressure transducer with a better accuracy.

242 From figure 10, which illustrates a comparison between the results obtained here and  
 243 those of Wegge *et al.*, it is possible to observe a significant negative relative deviation.

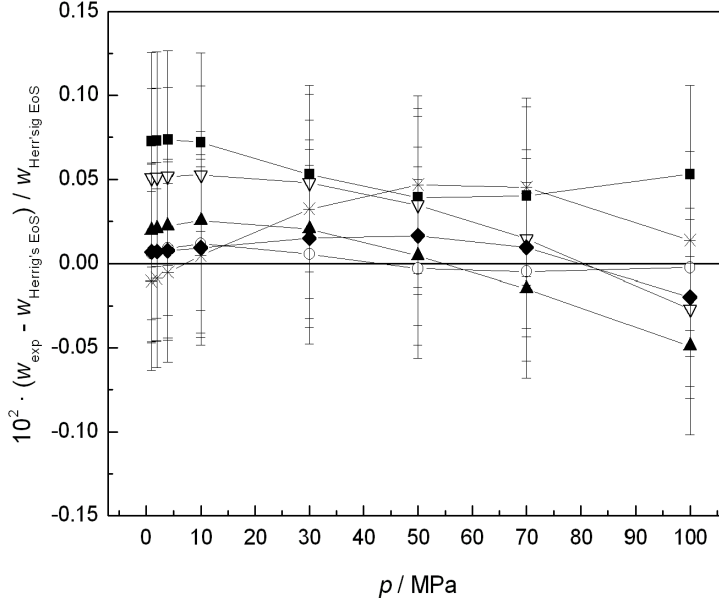


Figure 9. Relative deviation of experimental speed of sound results from Herrig’s EoS limited in pressure to 100 MPa. Symbols belong to (■) 297.97 K; (○) 283.15 K; (▲) 303.15 K; (▽) 323.15 K; (◆) 343.15 K; (\*) 363.15 K.

244 A possible explanation for the systematic deviation of these two measurements sets can  
 245 possibly ascribed to a different purity of the sample because the heavy water used in Wegge  
 246 *et al.* was pure at 99.995 % D atoms, while the purity of the sample used in this work was  
 247 only 99.85 % D atoms. Despite this significant purity difference, speed of sound results of this  
 248 work are still consistent with those of Wegge *et al.*, considering their combined uncertainties.  
 249 The only isotherm showing a significant deviation is that at the lowest temperature where,  
 250 probably, the effect of the contamination is enhanced by proximity to the freezing curve.

#### 251 IV. CONCLUSION

252 In this work, we report more than seventy experimental speed of sound measurements  
 253 in heavy water (deuterium oxide, D<sub>2</sub>O; purity: 99.85 %) on six isotherms between (276.97  
 254 and 363.15) K and, for the first time, for pressure up to 210 MPa. The results have been  
 255 obtained using the double *pulse-echo* technique and their estimated expanded relative com-  
 256 bined uncertainty ( $k = 2$ ) is, over the whole temperature range, in the order of 0.05 % for

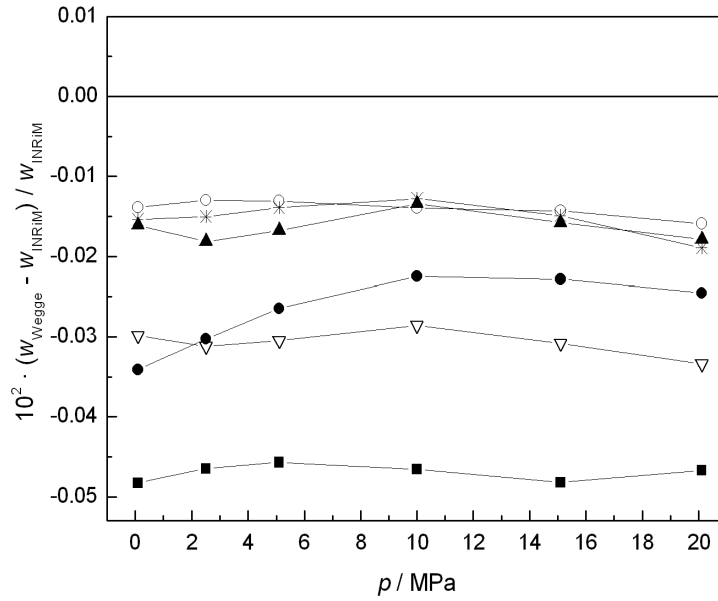


Figure 10. Comparison with the experimental speed of sound results of Wegge et al.<sup>5</sup> as a function of the pressure. Results are shown by isotherms: (■) 278.21 K; (○) 283.20 K; (▲) 293.20 K; (▽) 310.20 K; (●) 333.20 K; (\*) 353.20 K.

257 pressures above 10 MPa and of 0.03 % for pressures below 10 MPa. The obtained speed of  
 258 sound values have been compared with the predictions of the reference equation for heavy  
 259 water (IAPS84 Formulation) by Hill *et al.* (1982) and with those calculated from the newly  
 260 developed EoS for heavy water by Herrig *et al.* (2018), with resulting relative deviations  
 261 that are always less than the combined uncertainties. The speed of sound results have been  
 262 compared with the most recent results of Wegge *et al.* finding a remarkable agreement  
 263 within the declared uncertainty (better than 0.05 %).

264 Future work is planned to extend speed of sound measurements in deuterium oxide at  
 265 temperatures lower than the triple-point and for pressure up to 300 MPa. When available,  
 266 these results will be useful to update the recent dedicated EoS developed by Herrig *et al.*  
 267 (2018).

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