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<sup>1</sup> Speed of sound measurements in deuterium oxide ( $D_2O$ ) at temperatures between <sup>2</sup> (276.97 and 363.15) K and at pressures up to 210 MPa

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This paper presents speed of sound measurements in heavy water (deuterium ox-6 ide,  $D_2O$  along six isotherms between 276.97 K and 363.15 K for pressures up to 210 MPa using a double *pulse-echo* method. The experimental apparatus was val-8 idated measuring the speed of sound in ordinary water at ambient pressure and at 9 temperatures between 295.5 K and 363.15 K with results found in agreement with 10 values calculated from the reference equation of state for water by Wagner and Pruß 11 within 0.005 %. The relative combined expanded uncertainty of our speed of sound 12 measurements, at a confidence level of 95 %, is estimated to be less than 0.03 % for 13 pressures up to 10 MPa and in the order of 0.05 % for pressures up to 210 MPa in the 14 whole investigated temperature range. The speed of sound results have been com-15 pared with values calculated from the reference equation for heavy water the IAPS84 16 Formulation by Hill et al. (1982), and with the prediction of the newly developed 17 equation of state for heavy water by Herrig et al. (2018). The relative deviations 18 of these comparison were found to be consistent with the reference equations within 19 their combined uncertainty. The results presented here were also compared with the 20 most recent data by Wegge et al. and found to be in agreement within 0.05 %. 21

<sup>22</sup> Keywords: Speed of sound, deuterium oxide, heavy water, high pressure

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### 23 I. INTRODUCTION

Liquid deuterium oxide (often refered to as heavy water) is of interest in various scientific 24 fields for its <u>numeous</u> applications, e.g. to study mechanisms and rates of chemical or nuclear 25 reactions, for diagnostics in nuclear magnetic resonance, as well as in biological processes 26 and as coolant and moderator in pressurized heavy-water reactor (PHWR) of nuclear power 27 plants. A dedicated equation of state (EoS) is a useful tool to represent the ensemble of 28 thermodynamic properties needed to develop novel technological and industrial solutions. 29 The dedicated EoS of a fluid can reach high accuracy when also caloric properties (such as 30 speed of sound and specific heat capacity) are included in its implementation. High pressure 31 speed of sound measurements are of special interest because, being linked to both calorific 32 and mechanical properties of the fluid, they drive the choice of the number of terms that 33 are included in the equation of state and allow to improve its accuracy, and the physical 34 behaviour. Differently from the case of water, the thermodynamic properties of heavy water 35 are far less studied and measurements are usually affected by a larger uncertainty. The 36 measurement accuracy significantly improves for atmospheric pressure measurements and 37 a complete list of references of these measurements is reported in Table 13 of Herrig et38  $al.^1$  Anyway, since in this work the minimum pressure has been limited to 0.2 MPa (for 39 preventing the possible contamination of the fluid), a direct comparison with the results 40 reported at 0.1 MPa is not possible, unless by extrapolation. 41

Considering high pressure speed of sound measurements the availability of published 42 papers reduces to few works. In this case, mention is worth for the speed of sound results 43 obtained by Wilson<sup>2</sup> or by Chen and Millero<sup>3</sup> up to 100 MPa, those obtained by Aleksandrov 44 and  $\text{Larkin}^4$ , and the very accurate values by Wegge, Richter and Span  $(2016)^5$ . Some of 45 these data have been used by Hill *et al.*<sup>6</sup> to implement a fundamental equation of state, any-46 way that equation has a limited range of validity with a lower limit temperature of 276.97 K 47 and a maximum pressure of 100 MPa. More recently, a more accurate reference equation 48 of state has been implemented by Herrig  $et al.^{1}$ , but a definitive uncertainty estimation for 49 pressures above 100 MPa is not possible, because speed of sound data were not available in 50 this high pressure region. Motivated by this limited framework, we carried out more than 51 seventy experimental speed of sound measurements in heavy water (deuterium oxide,  $D_2O$ ; 52 purity: 99.85 % D atoms, deuterium atoms fraction), as reported and discussed in the rest 53

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

#### 59 II. EXPERIMENTAL SECTION

Speed of sound was measured by a double *pulse-echo* ultrasonic technique. The core 60 of the experimental apparatus, used for the determination of the phase velocity of the 61 ultrasonic waves, is a cylindrical stainless steel cell supplied with two reflectors placed at 62 unequal distances from a single piezoelectric transducer. The main features of the apparatus 63 design (with regard to the dimensions, constructing materials, gaskets, and because of the 64 absence of moving parts) make it a versatile instrument which can be operated over a wide 65 range of temperatures and pressures. The double *pulse-echo* method is based on direct 66 measurement of the time delay between echoes coming from the different reflectors. In a 67 previous paper<sup>7</sup>, details about the ultrasonic cell and the associated experimental apparatus 68 are provided. The adopted measurement design allows to compensate the effects due to 69 the trigger and electrical line delays but, even more importantly, this configuration allows 70 to obtain a repeatability of the time-of-flight measurements in the order of 10 parts per 71 million since tone bursts have very similar shapes. In figure 1, a geometrical sketch of 72 the measurement cell is shown. The nominal lengths of the spacers, separating the source 73 (red) from the reflectors are  $L_1 = 45$  mm and  $L_2 = 67.5$  mm. The acoustic path length was 74 estimated by the results of a calibration based on speed of sound measurements in high-purity 75 ordinary water  $(H_2O)$  at seven different temperatures (295.5, 303.15, 304.0, 319.0, 323.15, 76 343.15, 363.15) K and ambient pressure, with reference speed of sound values obtained from 77 the IAPWS-95 formulation<sup>8</sup>. 78

Additional experimental tests have been carried out to verify that calibrated  $\Delta L$  ( $\Delta L = L_2 - L_1$ ) did not vary, depending on the carrier frequency adopted to generate the signal. Three different runs have been performed using tone-burst of 5 cycles with a carrier frequency of 4 MHz and three additional runs with a carrier frequency of 8 MHz. Since the frequency 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	$2\Delta L \ / \ { m mm}$	$2\Delta L \ / \ { m mm}$	Relative	$2\Delta L \ / \ { m mm}$
$T = 294.95 { m K}$	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.

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

The relative deviations of our experimental results  $(w_{\text{INRiM}})$  from  $w_{\text{EoS}}$ , such as the speed of sound values calculated with the equation of state (EoS) of Wagner and Pruß<sup>8</sup>, are 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.

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

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

$$w_{\rm exp} = \frac{2\Delta L}{\tau_{\rm exp}},\tag{1}$$

where  $\Delta L$  is the difference in the acoustic paths travelled by the first two echoes coming from different reflectors and  $\tau_{exp}$  is the corresponding time delay. The time delay is determined 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

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

$$C(\tau) = \int_{-\infty}^{\infty} P_1(t) P_2(t+\tau) \mathrm{d}t, \qquad (2)$$

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

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



Figure 4. Wide-band ceramic PZT "DuraAct" kapton encapsulated.

$$w_{\rm exp} = \frac{2\Delta L}{\tau_{\rm exp} + \delta \tau},\tag{3}$$

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

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

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

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

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

measured by means of two PT100 thermometers inserted in the top and the bottom ends of 136 the pressure vessel. These thermometers were calibrated in the range of (230 and 390) K by 137 comparison with INRiM's (Istituto Nazionale di Ricerca Metrologica) Standard Platinum 138 Resistance Thermometer (SPRT) directly traceable to the National Temperature Standard. 139 A liquid bath thermostat maintains the temperature of experiment with a long term 140 stability better than  $\pm 1$  mK, over the whole working range, and is composed by a primary 141 external thermostat that can reach a stability of 10 mK and a secondary Proportional 142 Integrative and Derivative control (PID), providing feedback to achieve a finer temperature 143 control. 144

### <sup>145</sup> A. Preparation of the apparatus

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

Product name:	Deuterium Oxide, 99.9 % D atoms	Molecular Formula:	$D_2O$
Molecular Weight:	20.03	Assay (Quantitative NMR):	99.90 % D atom
Appearance (color):	colourless	Apprearance (form)	Liquid

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

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

The sample of deuterium oxide  $(D_2O)$  was supplied by Sigma-Aldrich. The declared spe-169 cific mole fraction purity of this sample was better than 99.9 % D atoms. No further analysis 170 or purification was attempted. Some cautions have been taken to try to preserve the purity of 171 the sample. For example, to limit the contamination due to air humidity, bottles have been 172 opened in a climatic room with relative humidity, at ambient temperature, below 20 % and 173 sealed with a valve immediately afterwards. Specification of the used  $D_2O$  sample has been 174 reported in table II, as declared by the supplier. Despite taken precautions, density changes 175 have been observed when the sample has been analyzed after speed of sound measurements 176 had been carried out. For this reason, the speed of sound results have been associated to a 177 composition in between the two compositions (99.85 % D atoms) and a further contribution 178 to the uncertainty budget has been added for accounting of the uncertainty of the sample 179 composition. 180

# <sup>181</sup> III. SPEED OF SOUND RESULTS AND COMPARISON WITH <sup>182</sup> EQUATION OF STATE PREDICTIONS

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

Source of uncertainty	Relative uncertainty Relative uncertainty		
	( <i>p</i> < 210 MPa)	( <i>p</i> < 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.

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

$T \ / \ \mathrm{K}$	$p \ / \ { m MPa}$	$w_{ m exp} \ / \ { m m \ s}^{-1}$
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

$T \mid K$	$p \ / \ { m MPa}$	$w_{ m exp} \ / \ { m m \ s}^{-1}$
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

$T \ / \ \mathrm{K}$	$p \ / \ { m MPa}$	$w_{ m exp} \ / \ { m m \ s}^{-1}$
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  $(w_{exp})$  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  $u(w_{exp}) = \pm 0.03$  % for pressure below 10 MPa and  $u(w_{exp}) = \pm 0.05$  % 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: ( $\blacksquare$ ) 276.97 K; ( $\bigcirc$ ) 283.15 K; ( $\bigstar$ ) 303.15 K; ( $\bigtriangledown$ ) 303.15 K; ( $\bigtriangledown$ ) 343.15 K; ( $\bigstar$ ) 363.15 K.

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

The experimental results obtained in this work were not used to implement the today most updated fundamental equation of state for heavy water (IAPWS-2017) by Herrig *et*  $al.^{1}$  and maintained by the International Association for the Properties of Water and Steam. Considering that the here obtained speed of sound measurements carried out are independent from those formulations, the comparison with IAPWS-2017 predictions and with the previous equation by Hill *et al.*<sup>6</sup>, gives an insight into improvements made by updating the 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: (×) 0.1 MPa; ( $\blacksquare$ ) 1 MPa; ( $\bigcirc$ ) 2 MPa; ( $\blacktriangle$ ) 4 MPa; ( $\bigtriangledown$ ) 10 MPa; ( $\blacklozenge$ ) 30 MPa; ( $\triangleleft$ ) 50 MPa; ( $\blacktriangleright$ ) 70 MPa; ( $\bigstar$ ) 100 MPa; ( $\bigstar$ ) 130 MPa; ( $\bigstar$ ) 160 MPa; ( $\bigoplus$ ) 180 MPa; ( $\Box$ ) 200 MPa; ( $\ast$ ) 210 MPa

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

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



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 ( $\blacksquare$ ) 297.97 K; ( $\bigcirc$ ) 283.15 K; ( $\bigstar$ ) 303.15 K; ( $\blacktriangledown$ ) 323.15 K; ( $\bigstar$ ) 343.15 K; ( $\ast$ ) 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.

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



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 ( $\blacksquare$ ) 297.97 K; ( $\bigcirc$ ) 283.15 K; ( $\bigstar$ ) 303.15 K; ( $\bigtriangledown$ ) 323.15 K; ( $\bigstar$ ) 343.15 K; ( $\bigstar$ ) 363.15 K.

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

From figure 10, which illustrates a comparison between the results obtained here and 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.

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

### 251 IV. CONCLUSION

In this work, we report more than seventy experimental speed of sound measurements in heavy water (deuterium oxide, D<sub>2</sub>O; purity: 99.85 %) on six isotherms between (276.97 and 363.15) K and, for the first time, for pressure up to 210 MPa. The results have been obtained using the double *pulse-echo* technique and their estimated expanded relative combined 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: ( $\blacksquare$ ) 278.21 K; ( $\bigcirc$ ) 283.20 K; ( $\blacktriangle$ ) 293.20 K; ( $\bigtriangledown$ ) 293.20 K; ( $\bigtriangledown$ ) 310.20 K; ( $\bigcirc$ ) 333.20 K; ( $\ast$ ) 353.20 K.

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

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

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