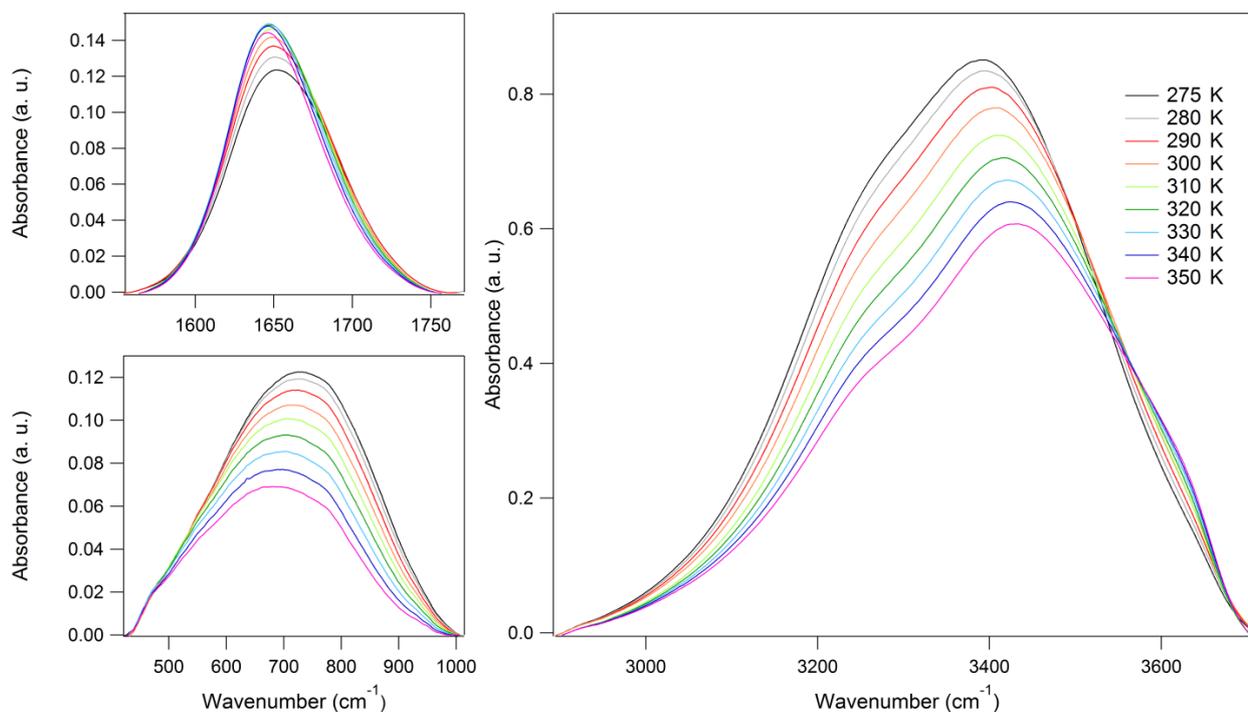
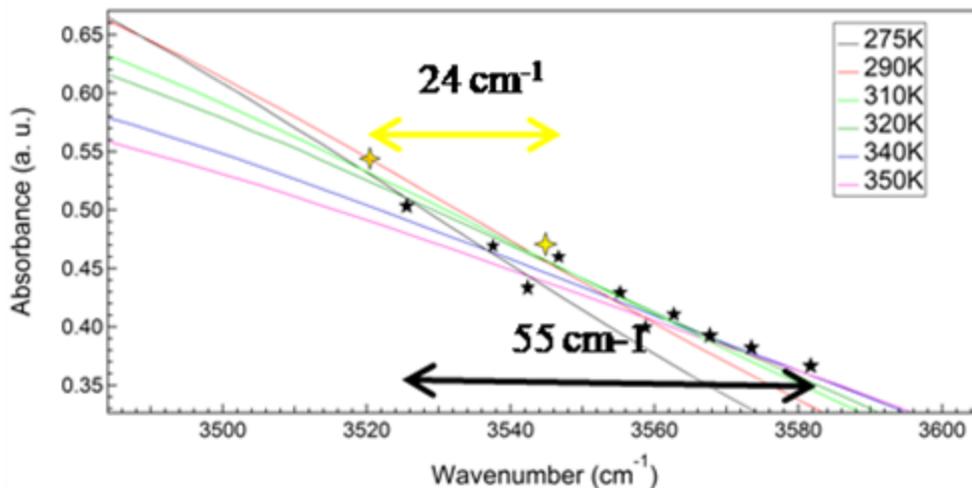


17 Finally, an isobestic-type crossing zone is displayed at high frequencies (see Fig A3), in the same
18 thermal range for the two experiments. The temperature at which this quasi-isobestic point
19 disappears is 310K for the AILES dataset, and 313K for the ISTO dataset, in good mutual
20 agreement.

21 The bending band (Fig. A1) exhibits an increasing absorbance with temperature, and the maximum
22 slightly shifts toward lower wavenumbers from 1650.7 cm^{-1} at 263K to 1648.3 cm^{-1} at 363K
23 (experiment under atmospheric conditions) and from 1651.7 cm^{-1} at 275K to 1646 cm^{-1} at 350K
24 (experiment under vacuum). The band shape never changes with temperature, except for a
25 decreasing FWHM and an increasing absorbance, both observed onto the two datasets.



26
27 Figure A2. OH stretching, bending and libration bands as a function of temperature, acquired with
28 the AILES setup, under vacuum (see section 3.2). Due to the experimental condition, the libration
29 band is restricted at 426 cm^{-1} .



30

31 Figure A3: Zoom on the quasi isobestic spectral domain (spectra measured under vacuum). The
 32 black stars indicate the “isobestic crossings” above 313K, while the yellow stars materialize
 33 “isobestic crossings” below 313K.

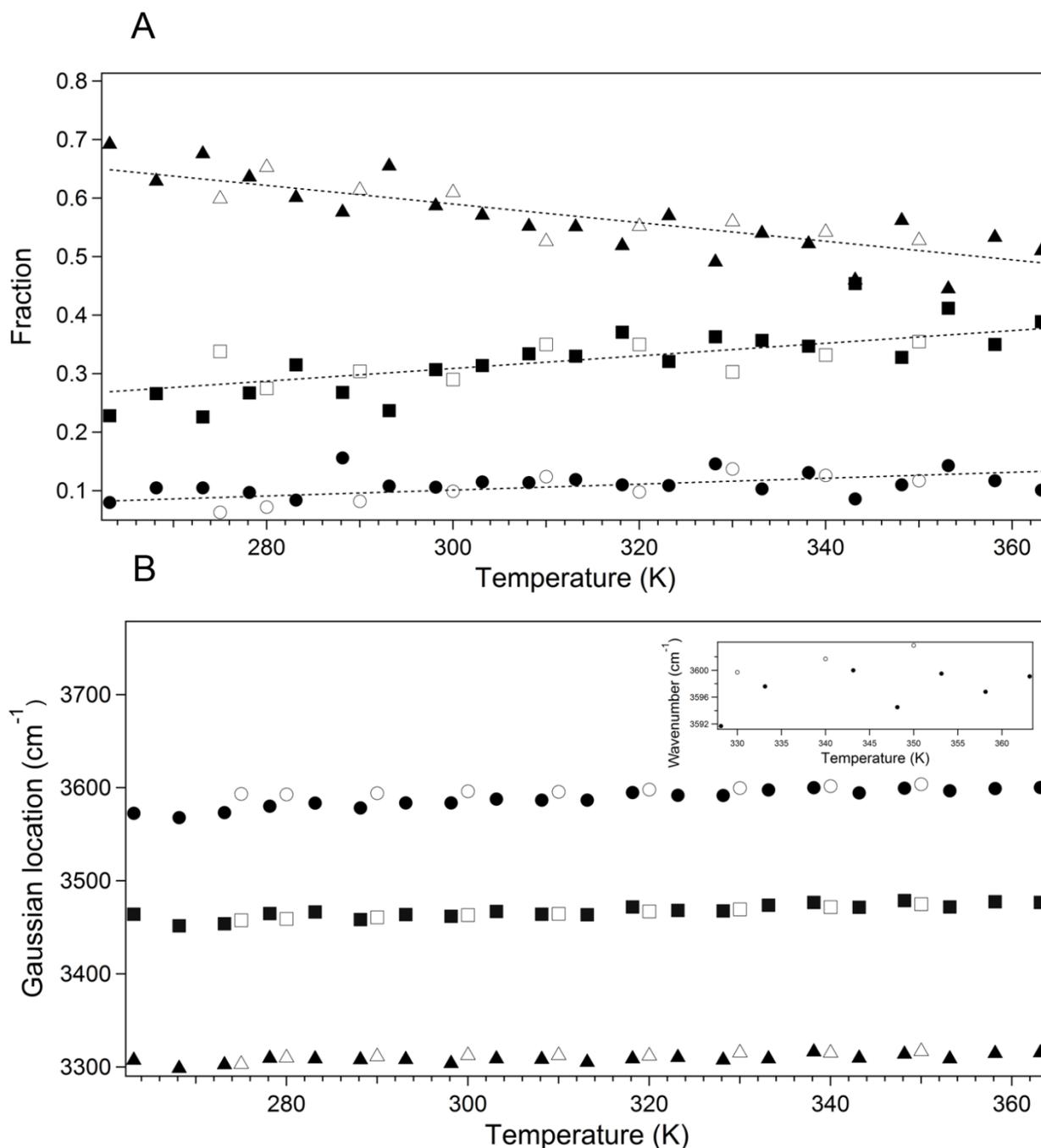
34 The decomposition of the OH stretching band into three Gaussian components, ascribed to water
 35 molecules with a given coordination number (NW, IW and MW), enables to refine the inter-
 36 comparison. Table A1 presents the molecular fraction and the frequency of the sub-bands at 263K
 37 and 363K obtained with the ISTO setup.

38 Table A1. Molecular fractions and main peak location of the sub-bands fitted on the OH-stretching
 39 band recorded as a function of temperature with the ISTO setup (in contact with atmosphere).

Water classes	Temperature	Molecular fractions	Main peak frequency (cm ⁻¹)
NW	263.15K	0.692	3307
	363.15K	0.510	3315
	Variation	-0.182%/K	+0.08 cm⁻¹/K
IW	263.15K	0.228	3464
	363.15K	0.389	3477
	Variation	+0.161%/K	+0.13 cm⁻¹/K
MW	263.15K	0.08	3572
	363.15K	0.101	3600

Variation	+0.021%/K	+0.28 cm⁻¹/K
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40 Table 1 in the main text gives the same information recorded with the AILES setup, comparing the
41 trends between the two limit temperatures, 275K and 350K. Both datasets evidence that the NW
42 population is dominating along the temperature range but decreases with temperature, while both
43 the IW and MW populations increase with temperature (Tables A1 and 1, and Figure A4).
44 Moreover, the positions of the three Gaussians are also slightly shifted toward higher frequencies
45 with the increasing temperature, and the most pronounced move is observed for MW, the minor one
46 for NW (Table A1 and figure A4). The only exception for this regular behavior is given by MW
47 calculated from the data over 275-350K, most probably due to the absence of measurements in the
48 last 10K, whose slope is markedly increasing on the other dataset (Fig. A4 B).
49 Both datasets appears completely consistent, especially with regards to features supporting the
50 thermodynamic interpretation. That leads to conclude that the water spectra obtained with usual
51 laboratory spectrometer can serve to calculate thermodynamic properties of liquid water.



52

53 Figure A4. A. Molecular fractions of the three water populations as a function of temperature. B.

54 frequency of each sub-band as a function of temperature. Circle: MW, Square: IW and Triangle:

55 NW. Filled symbols, ISTO measurements; empty symbols, AILES measurements.