Supplementary Material for: "Quantitative rotational to librational transition in dense H_2 and D_2"

Miriam Peña-Alvarez,[*,†] Veronika Afonina,[†] Philip Dalladay-Simpson,[‡] Xiao-Di Liu,[¶] Ross T. Howie,[‡] Peter I. C. Cooke,[†] Ioan B. Magdau,[†,§] Graeme J. Ackland,[†] and Eugene Gregoryanz[*,‡,†,¶]

†*Centre for Science at Extreme Conditions & The School of Physics and Astronomy, The University of Edinburgh, Peter Guthrie Tait Road, Edinburgh, EH9 3FD, U.K.*

‡*Center for High Pressure Science & Technology Advanced Research, 1690 Cailun Road, Shanghai, 201203, P. R. China*

¶*Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, P. R. China*

§*Department of Chemistry and Chemical Engineering, California Institute of Technology, U.S.A.*

E-mail: mpenaal@ed.ac.uk; e.gregoryanz@ed.ac.uk

Methods

For this study, we conducted a total of 10 independent experiments. The pressure-temperature (P-T) space covered was between 300, 150, 80, and 10 K and from 0.2 to 150 GPa. We have generated high pressures in the long piston-cylinder and symmetric diamond anvil cells of our design with diamonds having culet sizes from 50 to 200 μm. We have used rhenium foils of 200-250 microns thick as a gasket material. The hydrogen (deuterium) gas was clamped at 1850-2000 bar and pressurised to 1-2 GPa while in the gas loader. The cell was mounted into the custom-built cryostat which allows conducting *in situ* optical measurements from 300 to 5 K. The Raman spectra were excited using 532 and 514 nm excitations wavelengths and collected with a spectrograph equipped with charge coupling device (CCD) array detector.

Pressures were measured cross-referencing the diamond edge scale,[1] the luminescence of ruby.[2] At room temperature, the pressure was cross-referenced as well with the Raman shift of the H_2 and D_2 vibron.[3]

We examine how rotational peaks split with compression and if the splitting could be indicative not only of the field-effect induced by compression of the hexagonal structure but also of any roton-phonon coupling, hindering rotational motion. To homogenise the fitting of the spectra the background which increases with compression as resulting from diamond fluorescence was subtracted. We fit our experimental spectra into a sum of Voigt functions considering the splitting of the sublevels. All the analysis was done using the software called OriginLab.

Assignment of the contributions starts with the 10 K spectra where the different contributions are very well defined even without the need of second derivative analysis or support from theoretical data. Assignment of the $S_0(0)$ modes was an iteration process starting with the aid of the frequencies taken from the minima and the second derivative, which indicates that there are three contributions in the $S_0(0)$ supporting rotational quantum theory.[4,5] To calculate the second derivative in the cases of the noisiest spectra we conduct a smoothing with a standard smoothing procedure with a third-order polynomial function named Sav-

itzky–Golay smoothing with a length of about 5- 25 data points, increasing as the noise of the spectrum increases. The location of the second derivative minima is done visually and taken as a starting fitting parameter of the contributions.

We fitted each contribution to Voight shapes. We start our analysis with the results obtained at 10 K and the lowest pressure with the sharper contributions, which become our reference. Fittings are done through an iterative process, always including all the contributions and the phonon in the process. We continue the iterations until we get the best match between the spectral profile and our fitting function while minimizing the dispersion in the Raman shift, Full width half maximum, and areas vs pressure plot. All the plots here presented rotons intensities are normalized to the most intense roton to help visualization.

Iterative process in fittings. Taking the Raman shift values from the second derivative analysis we start by fitting the 10 K lowest pressure data. Then the results of this fitting are used as starting parameter in the next pressure step at the same temperature. The iteration is started fixing all the parameters, frequency, full width half maximum (FWHM) and area, then they are set free to iterate 1 to 1 until there are no changes in the iteration and there is a minimum difference between the calculated and experimental spectra. For the 80 K isotherm, at the lowest pressure the data obtained in the fittings from 10 K at the lowest pressures are used as initial FWHM and areas while using the as Raman shift initial constrains those obtained from the second derivative. Then for the next pressure steps, the values of FWHM and area of the pressure step below are used and the Raman shift of its own second derivative. The same for 150 K but using as reference of FWHM and area at the lowest pressure the values from 80 K at the lowest pressure, and analogously for 300 K but with 150 K as reference. Fittings are considered valid when convergence between the best calculated spectrum vs experiment is reached, while providing and smooth FWHM trends.

Contour plots. To generate the contour plot, we create a matrix $\omega_{H_2}/\omega_{D_2}$ from interpolation of the data within experimentally covered *Pressure-Temperature (P-T)* range.

1. From the linear fits of the ratio $\omega_{H_2}/\omega_{D_2}$ vs pressure, figure 4 of the main text, we take those lines and estimate for each temperature what the ratio would be for the pressures of interest in 5 GPa steps: 10 K up to 70 GPa, 80 K up to 100 GPa, 150 K up to 300 GPa and 300 K up to 300 GPa. Then we have created a matrix with 4 rows (1 per temperature) and 60 columns.

2. We represent the estimated $\omega_{H_2}/\omega_{D_2}$ ratios for each of the pressures vs temperature, we have 4 x values and 60 y columns. We fit our points to a third order polynomial, ratio vs temperature.

3. With the new curve we have obtained we can now estimate what the ratio would be for temperatures between 10 K and 300 K (in 5 K steps) and pressures up to 300 GPa. We create a matrix with the interpolated$\omega_{H_2}/\omega_{D_2}$ ratios: 58 (Temperature steps) x60 (pressure steps), this matrix is then used to draw the contour plot.

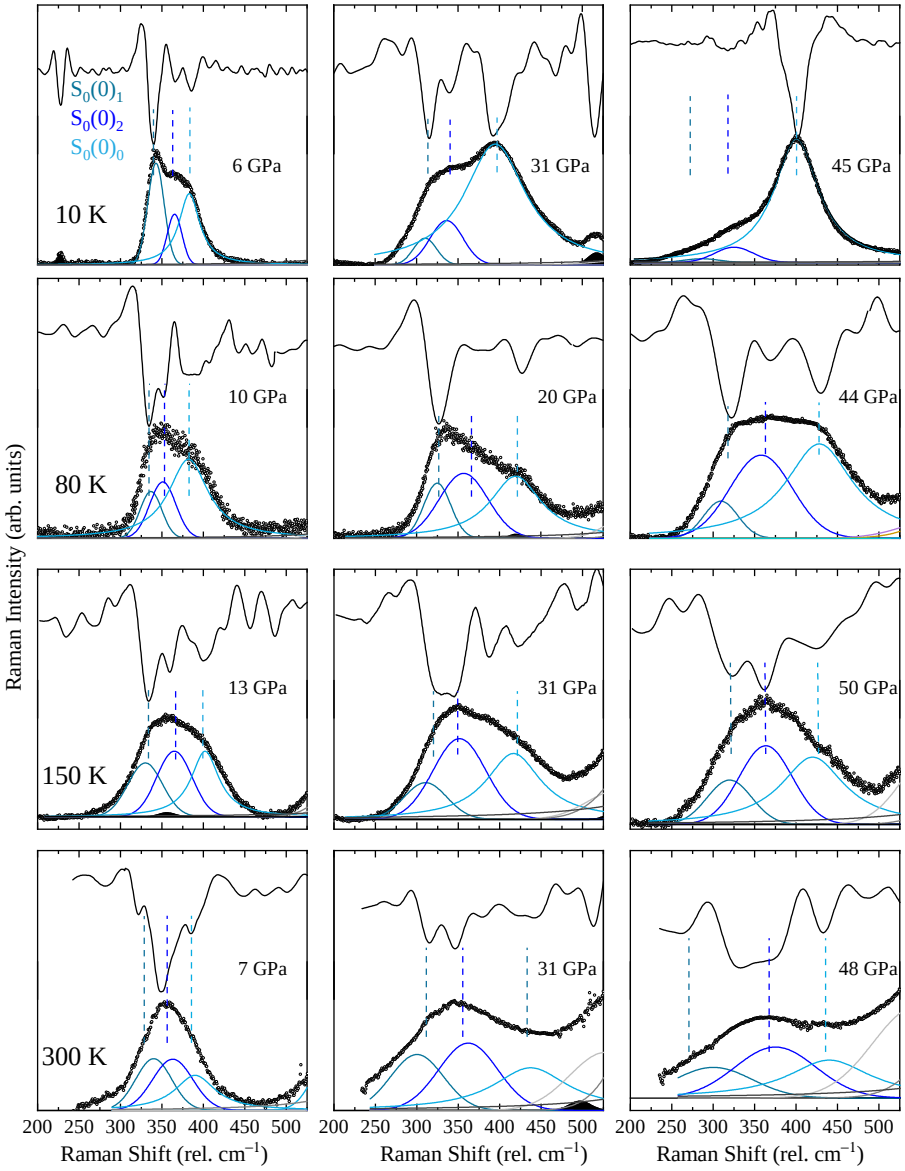

Figure S1: Representative with spectra (dotted) and their second derivative analysis (solid black line above each spectrum) for Hydrogen $S_0(0)$ rotons at 10, 80 150 and 300 K from bottom to top, at selected pressures. Dashed lines are used to assign the correspondence between the roton contribution and the derivative minimum. The fitted $S_0(0)_1$, $S_0(0)_2$, $S_0(0)_0$ contributions are included together with the spectra.

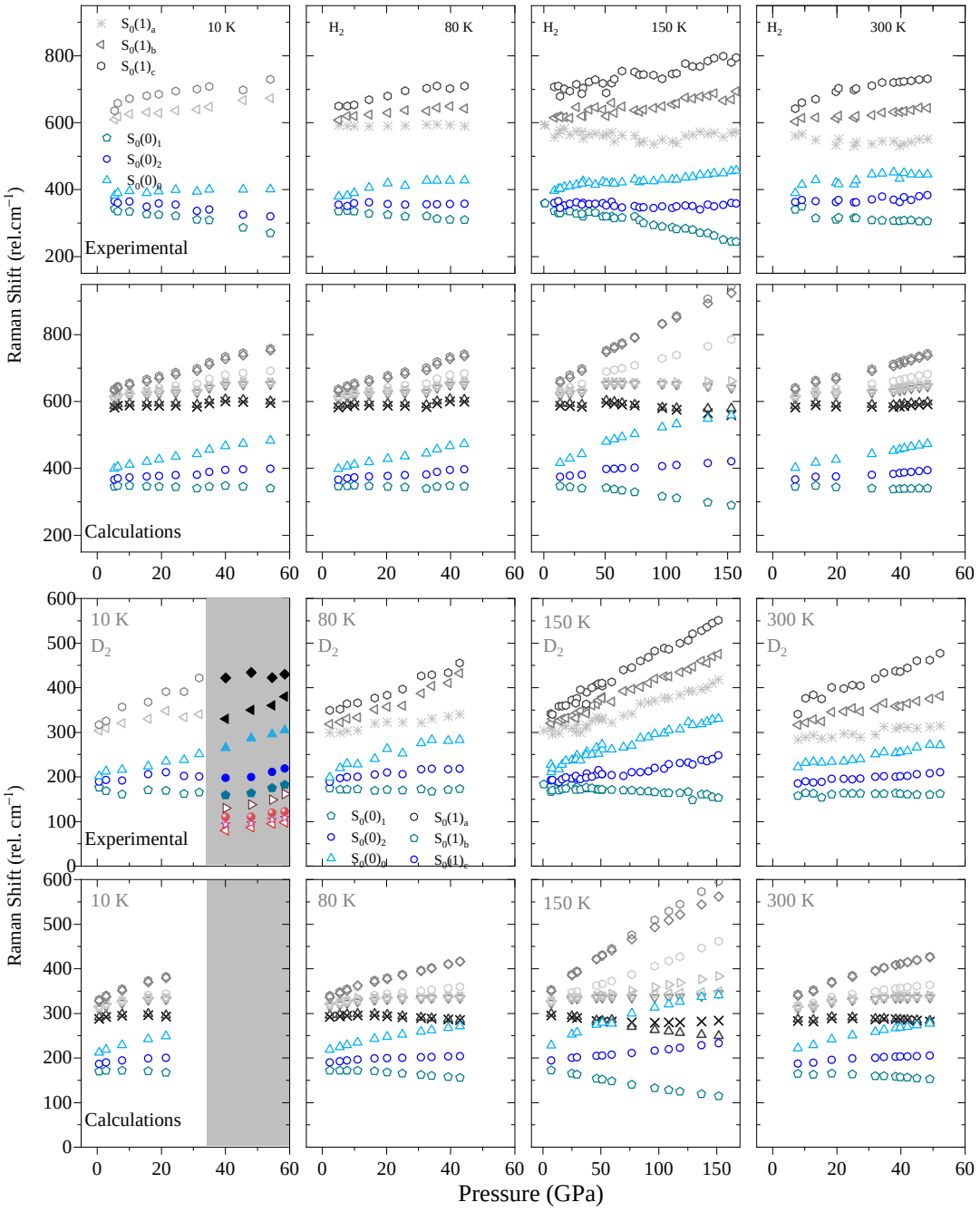

Figure S2: Raman shift for the $S_0(0)$ and $S_0(1)$ contributions as a function of pressure of: top H_2 experimental and theoretical from Cooke et al.[5] and bottom D_2 experimental and theoretical from Cooke et al.[5] 10 K D_2 phase II (II'[6]) region is marked with the shadowed area and filled symbols.

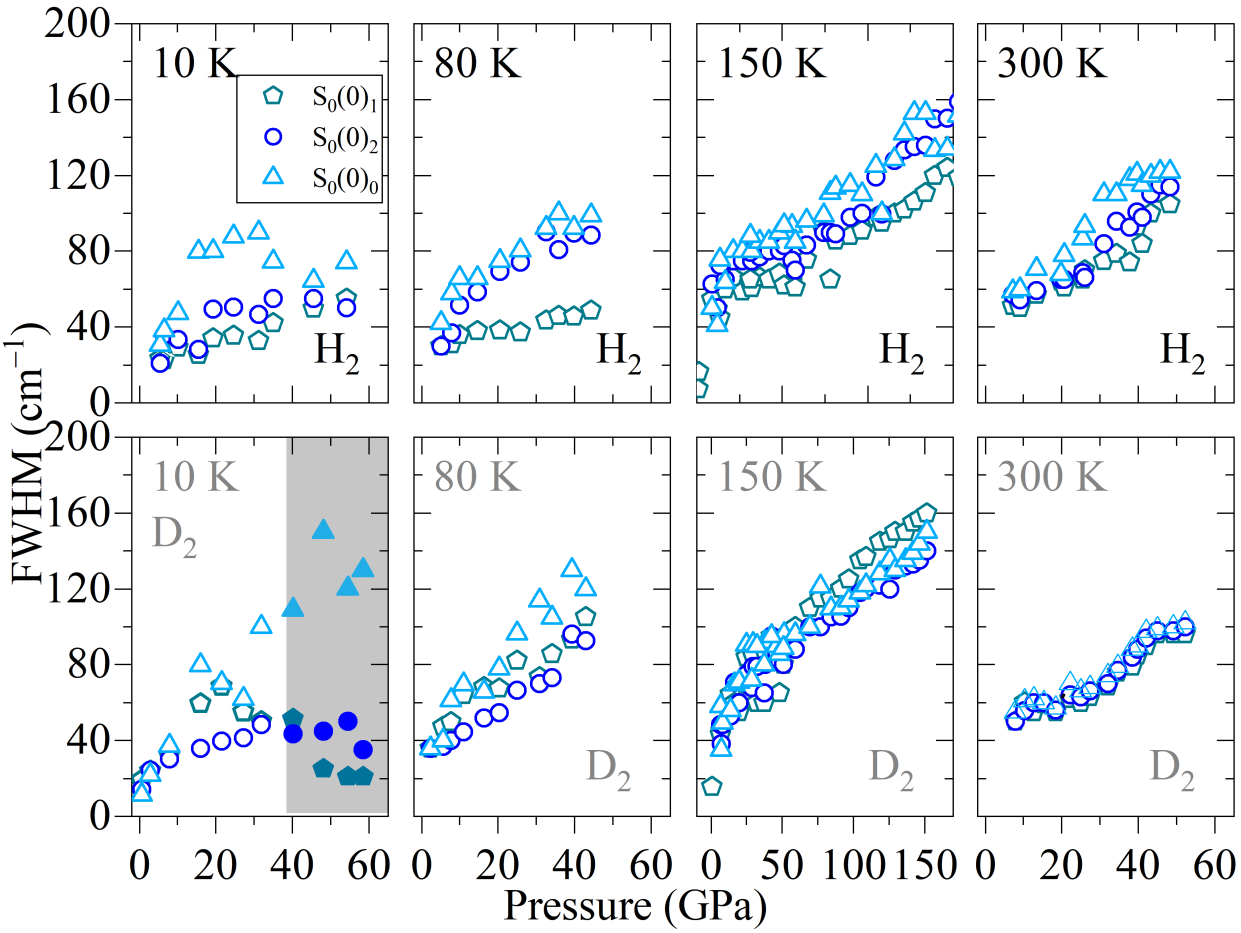

Figure S3: Full width half maximum for the $S_0(1)$ contributions as a function of pressure of H_2 (top panel) and D_2 (bottom panel). 10 K D_2 phase II region is marked with the shadowed area and filled symbols.

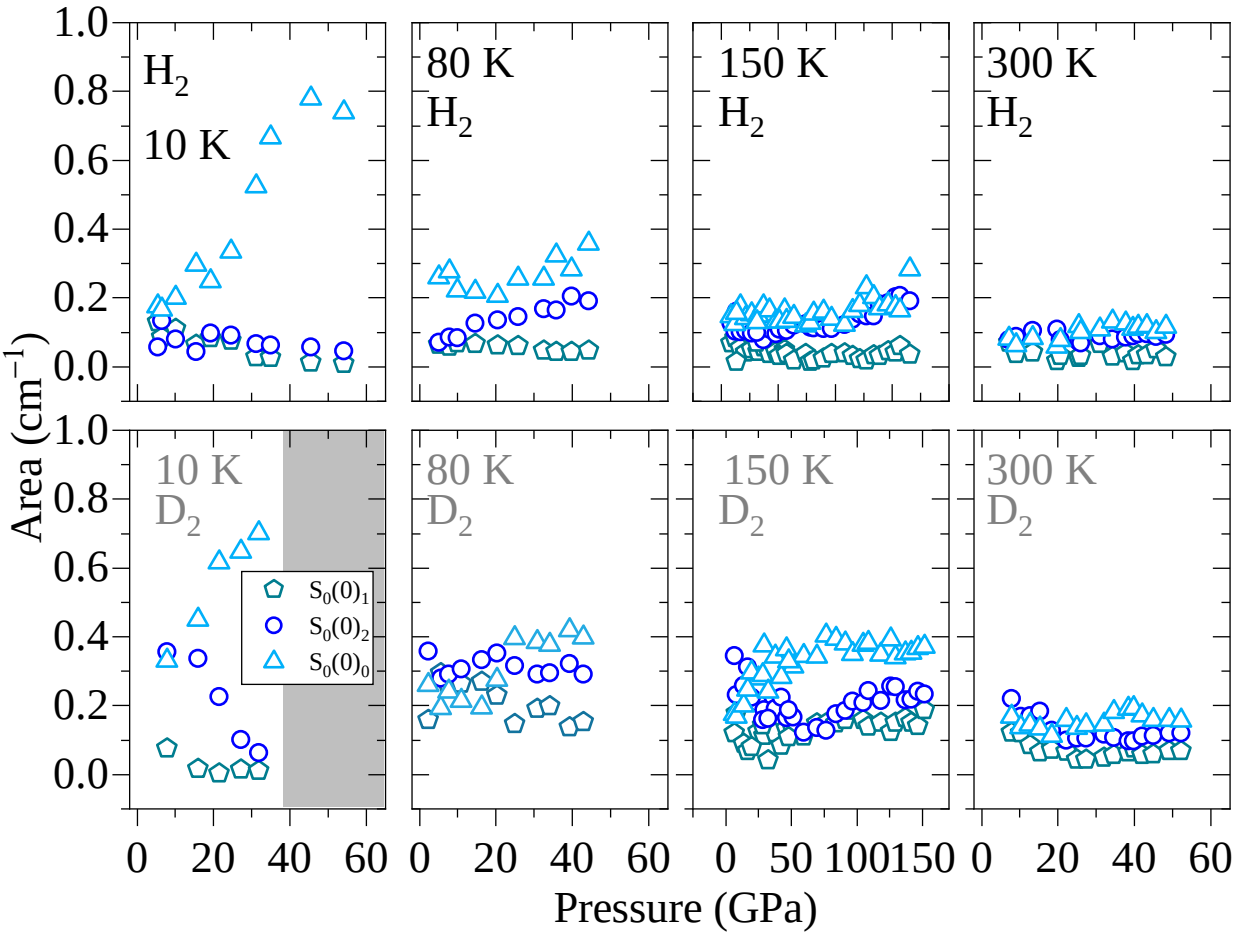

Figure S4: Area for the $S_0(0)$ contributions as a function of pressure normalised to the total area of the $S_0(0)$ and $S_0(1)$ bands: H_2 (top panel) and D_2 (bottom panel). 10 K D_2 phase II region is marked with the shadowed area and filled symbols. At 10 K for H_2 we see a fast growth of the $S_0(0)_0$ which results from the pressure enhanced *para-ortho* transition .[7] The ideal configuration for the (2:2:1) intensity ratio between the $S_0(0)_2$, $S_0(0)_1$, and $S_0(0)_0$ is altered, which has already been attributed to *ortho para* effects, and to crystal orientation, and to spectroscopic configuration.[4,5]

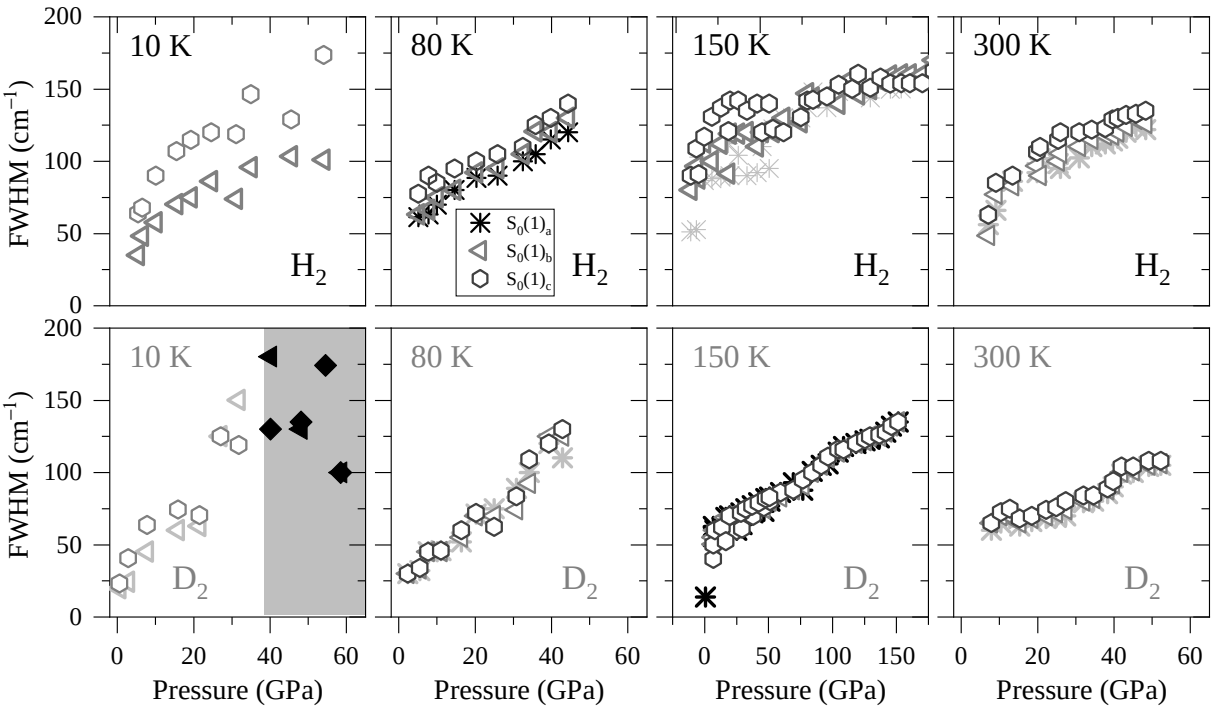

Figure S5: Full width half maximum for the $S_0(1)$ contributions as a function of pressure of: top H_2 and bottom D_2. 10 K D_2 phase II' region is marked with the shadowed area and filled symbols.

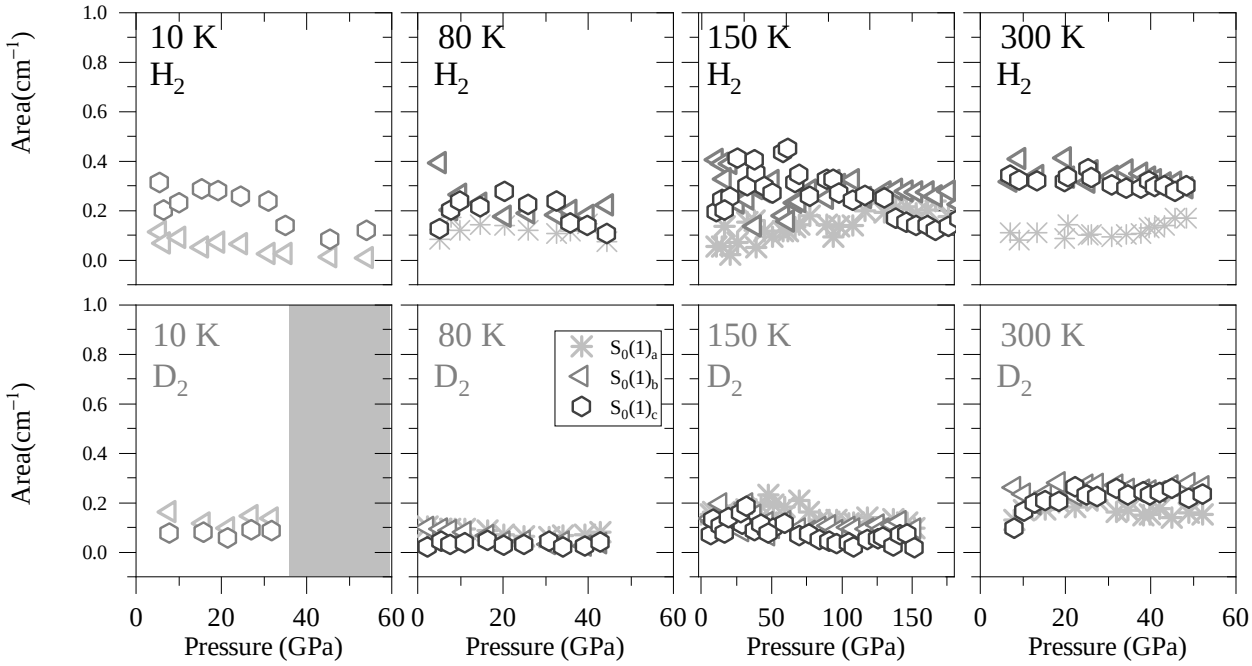

Figure S6: Area for the $S_0(1)$ contributions as a function of pressure normalized to the total area of the $S_0(0)$ and $S_0(1)$ bands. top H_2 and bottom D_2. 10 K D_2 phase II' region is marked with the shadowed area and filled symbols.

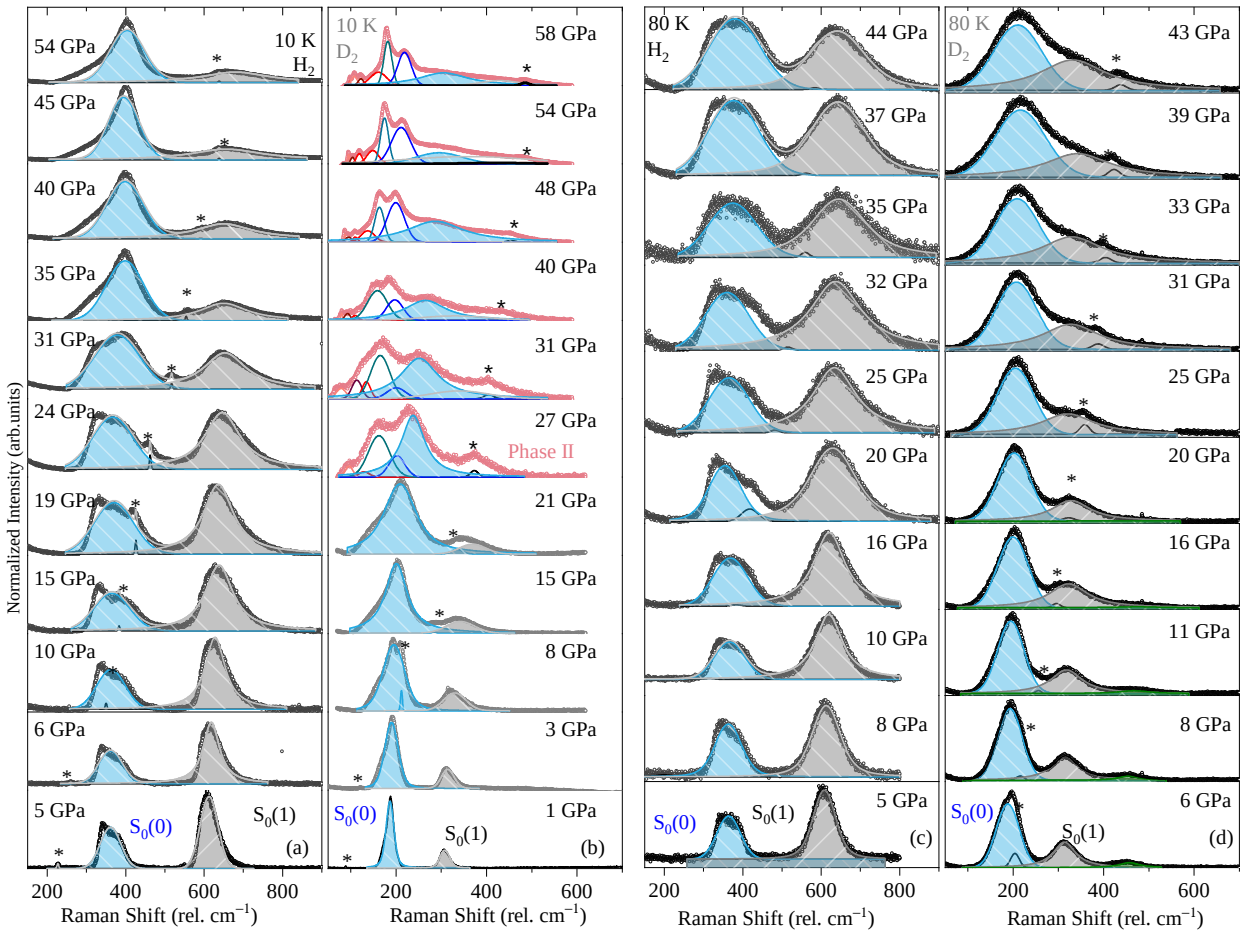

Figure S7: Representative Raman spectra during isothermal compression paths fitting $S_0(0)$ and $S_0(1)$ to Voight profiles as a single contribution. a) At 10 K to maximum pressure of 54-58 GPa of hydrogen; b) deuterium, which at 26 GPa undergoes a transition to phase II (II'[6]) marked by the new contributions in red. c) at 80 K up to 44 GPa of hydrogen; d) deuterium. Where visible, E_{2_g} phonon is marked with $*$ symbol.

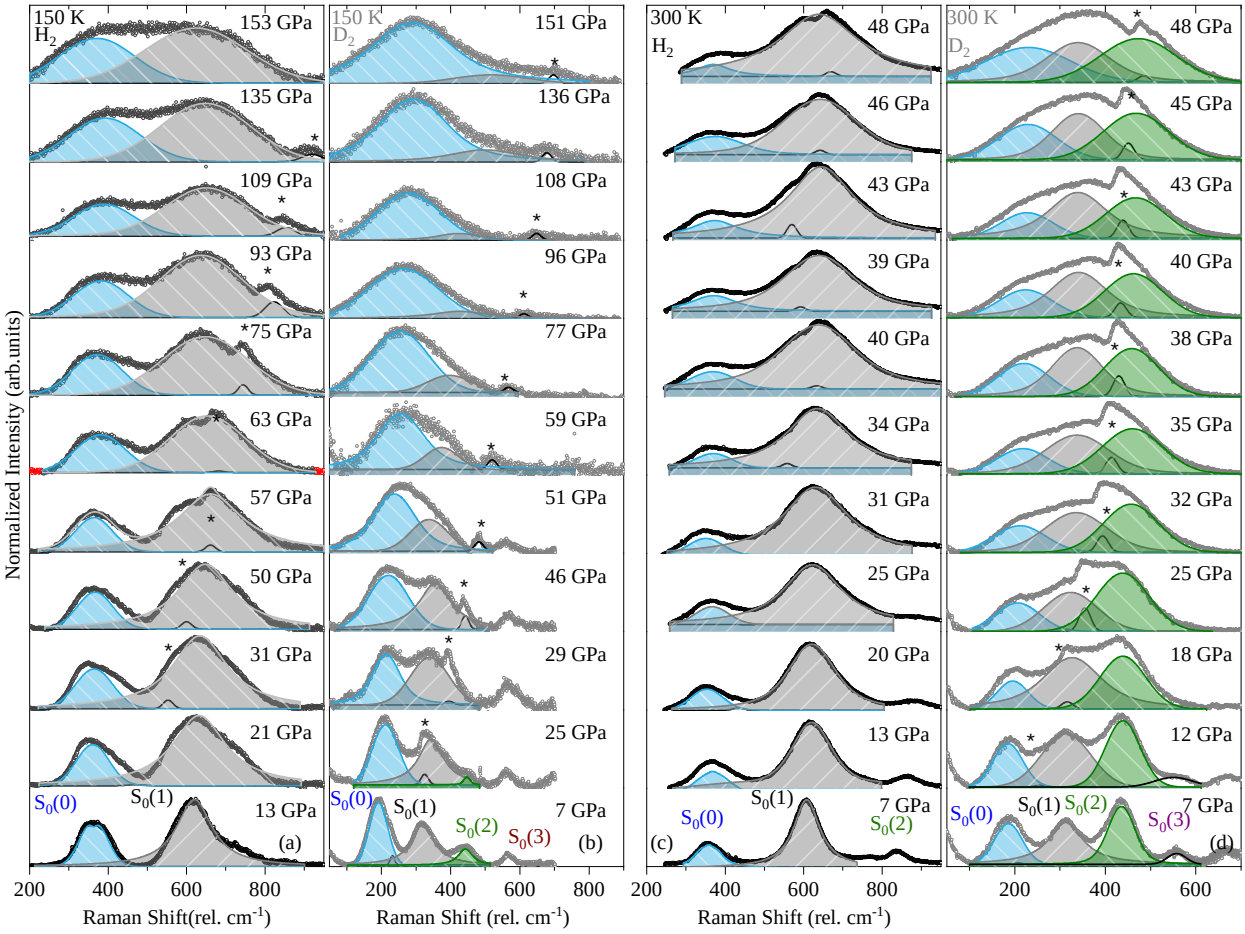

Figure S8: Representative Raman spectra during isothermal compression paths $S_0(0)$ and $S_0(1)$ and $S_0(2)$ (when populated) to Voight profiles. a) At 150 K to maximum pressure of 150 GPa of hydrogen; b) deuterium. c) At 300 K to a maximum pressure of 48 GPa of hydrogen; d) deuterium. Where visible, phonon E_{2g} mode is marked with * symbol, and it is shifting with pressure faster than rotational modes.

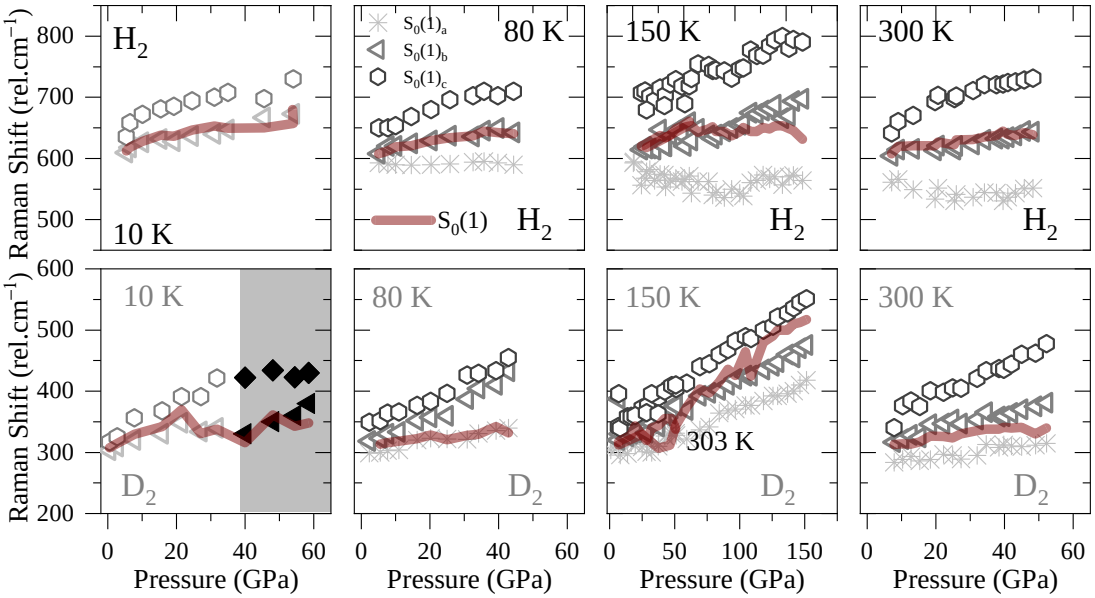

Figure S9: Raman shift of the $S_0(1)$ contributions as a function of pressure of: top H_2 and bottom D_2. 10 K D_2 phase II (II'[6]) region is marked with the shadowed area and filled symbols. Thick red line corresponds to the points obvained considering $S_0(0)$ as a single contribution (Figures S8-S9).

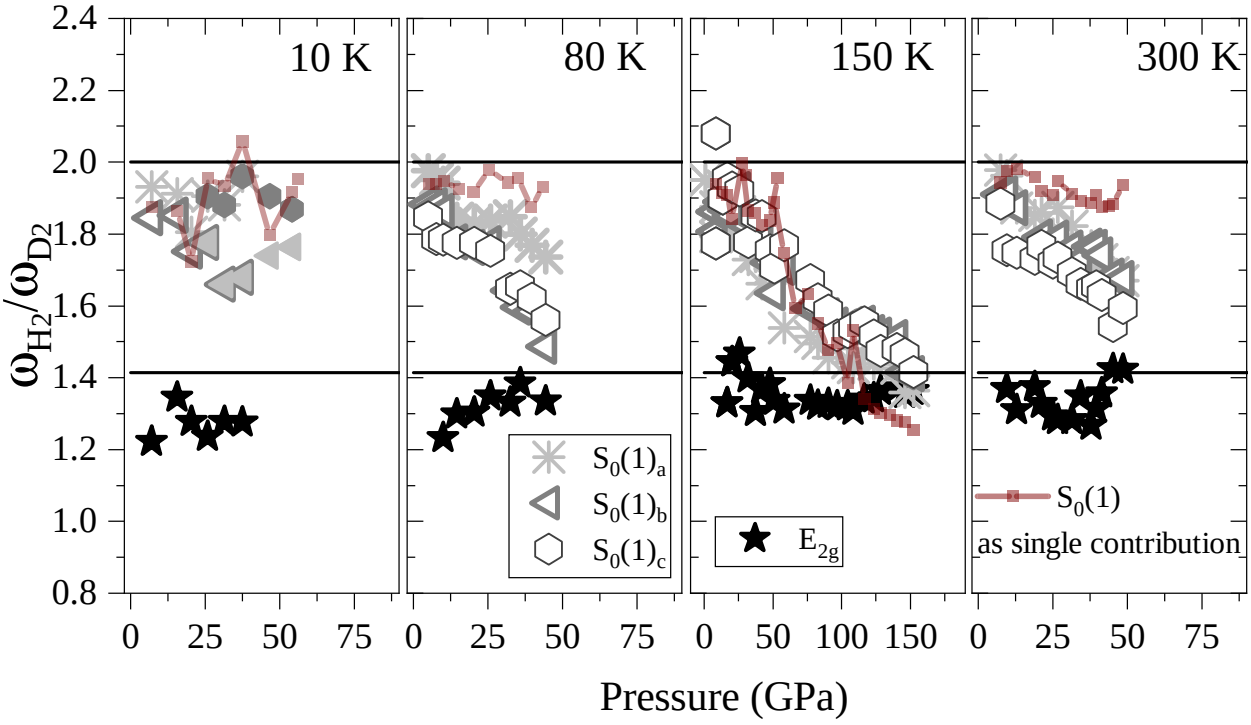

Figure S10: Pressure dependence of $S_0(1)$ ratios:$\omega_{H_2}/\omega_{D_2}$. Horizontal lines mark the ratio in a pure harmonic oscillator, at $\omega_{H_2}/\omega_{D_2} = \sqrt{2}$, and pure rigid rotor ratio $\omega_{H_2}/\omega_{D_2} = 2$. Red joined symbols correspond to the ratios calculated from Raman shifts of the $S_0(1)$ as a single contribution, Figure S8-S9 and S10.

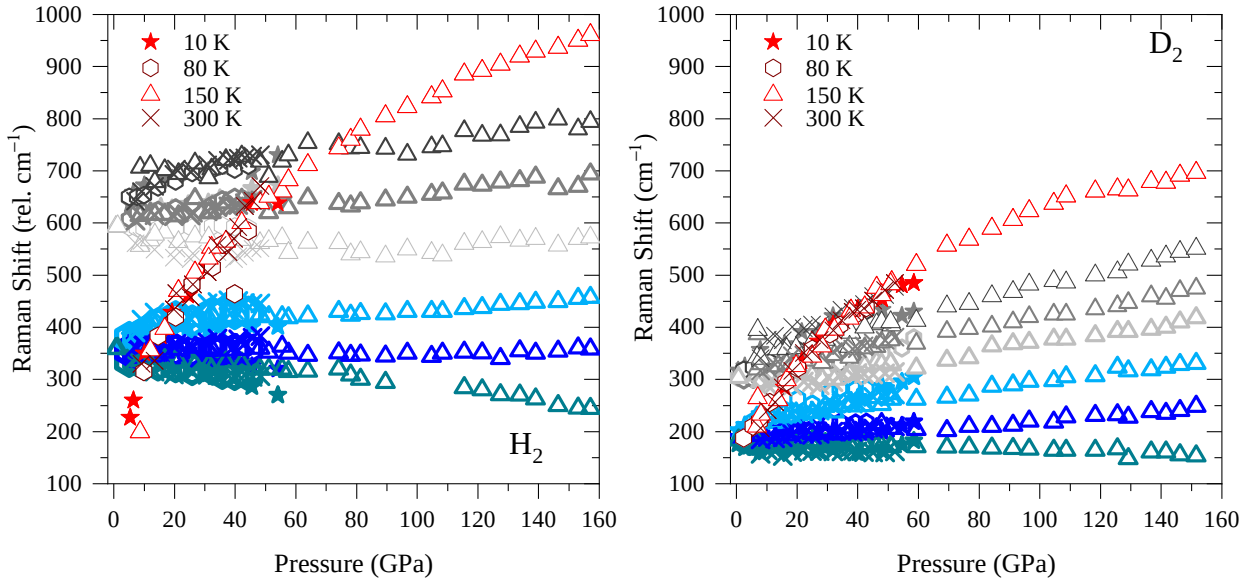

Figure S11: Raman shift for the E_{2_g} phonon in red, $S_0(0)$ in blue and $S_0(1)$ as a function of pressure of: left H_2 and right D_2.

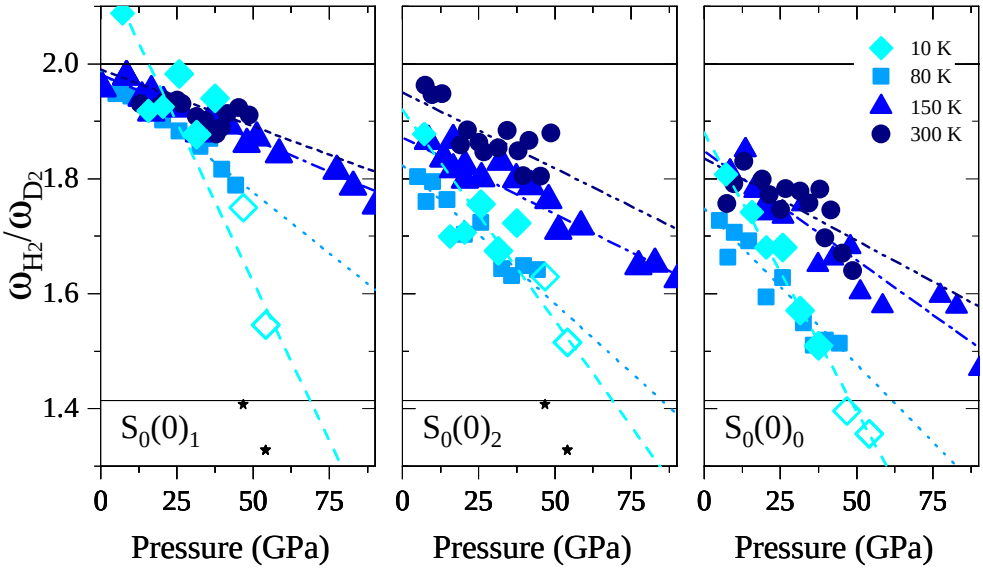

Figure S12: Pressure dependence of $S_0(0)$ ratios:$\omega_{H_2}/\omega_{D_2}$. Horizontal lines mark the ratio in a pure harmonic oscillator, at $\omega_{H_2}/\omega_{D_2} = \sqrt{2}$, and pure rigid rotor ratio $\omega_{H_2}/\omega_{D_2} = 2$. (a)$S_0(0)_1$; (b) $S_0(0)_2$; (c) $S_0(0)_0$. Empty cyan symbols correspond to the ratios considering D_2 phase II'.

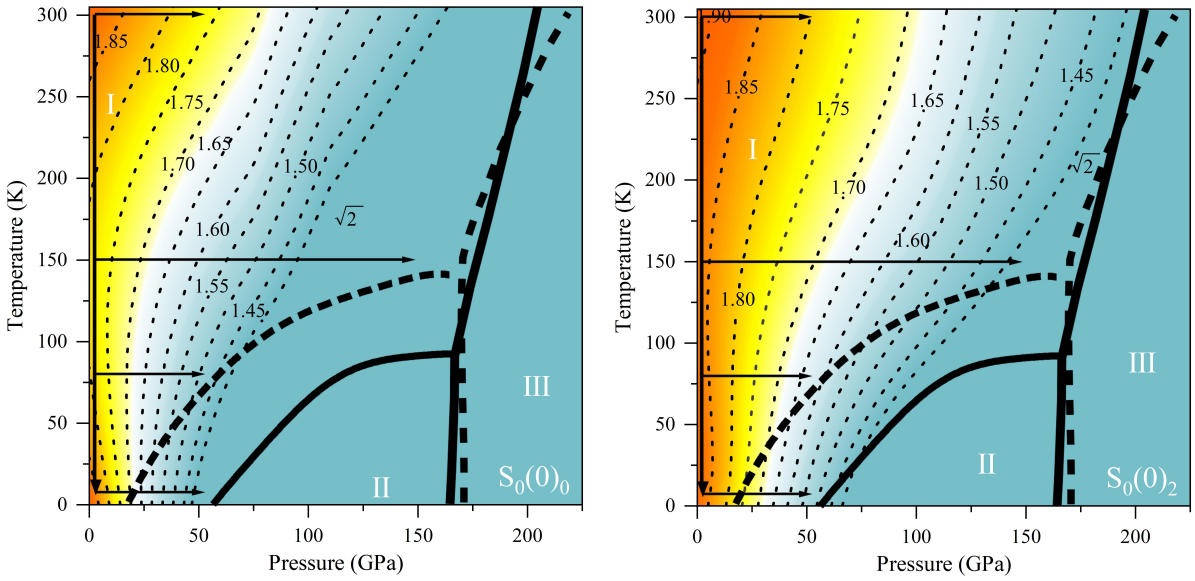

Figure S13: H_2 and D_2 phase diagrams represented with solid and dashed lines respectively, taken from Ref.[6] Contour curves represent the change in the $\omega_{H_2}/\omega_{D_2}$=2 to $\sqrt{2}$. Each panel gathers the results obtained for each of the $S_0(0)$ contributions, left: $S_0(0)_0$ and right: $S_0(0)_2$. Arrows are used to indicate the experimental paths followed here, typically cooling fast with a subsequent isothermal compression.

References

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