Supporting Material

Intra-cage Structure, Vibrations and Tetrahedral-Site Hopping of H_2 and D_2 in Doubly-Occupied $5^{12}6^4$ Cages in sII Clathrate Hydrate from Path-Integral and Classical Molecular Dynamics

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Accompanying Gaussian cube-file listing

cube5.cub: small-cage (dodecahedral) D2 density (classical)
cube6.cub: large-cage (5-12-6-4) D2 density (classical)
cube5p.cub: small-cage (dodecahedral) D2 density (path integral)
cube6p.cub: large-cage (5-12-6-4) D2 density (path integral)

Proton-Velocity Spectra

The proton-velocity spectra in both the lattice and guests are presented below, including for the deuterated cases, sampled from classically-propagated MD at 100 K. The frequency modes obey the expected isotope effect quite well, in that doubling the mass serves to reduce the observed frequency mode by √2. This is evident in Fig. S1c, where the frequencies of the deuterated spectra are scaled by √2.

Fig. 1 depicts the translational-librational region, whilst Fig. 2 shows the full frequency range (up to bond stretch). In both cases, the units are arbitrary on the ordinate axes.

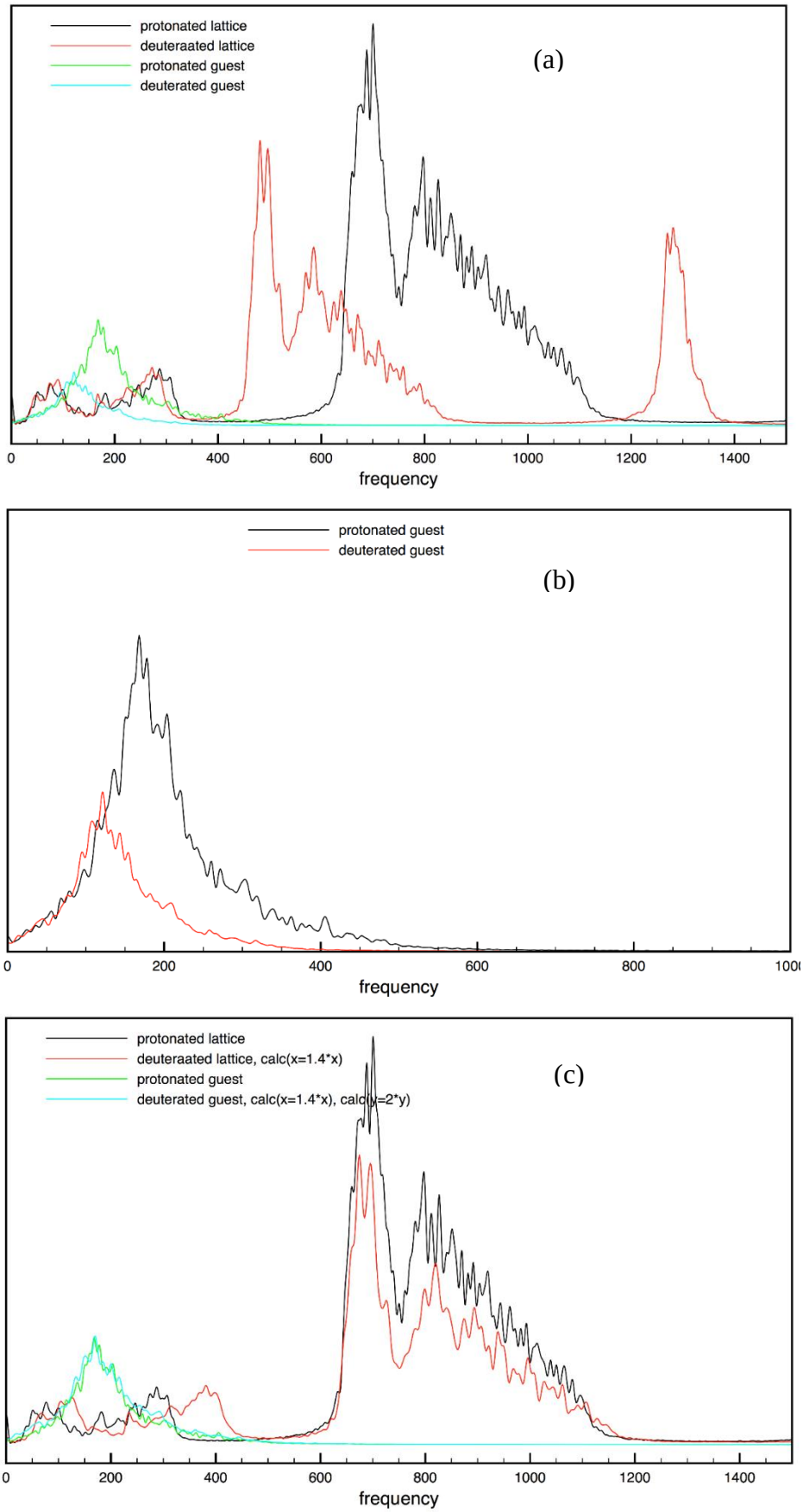

Fig. S1: Translational and librational region of the (a) lattice and (b) guest proton-velocity spectra. In (c), there is scaling by a factor of √2 applied for the duterated spectra, indicating the expected isotopic vibrational effect.

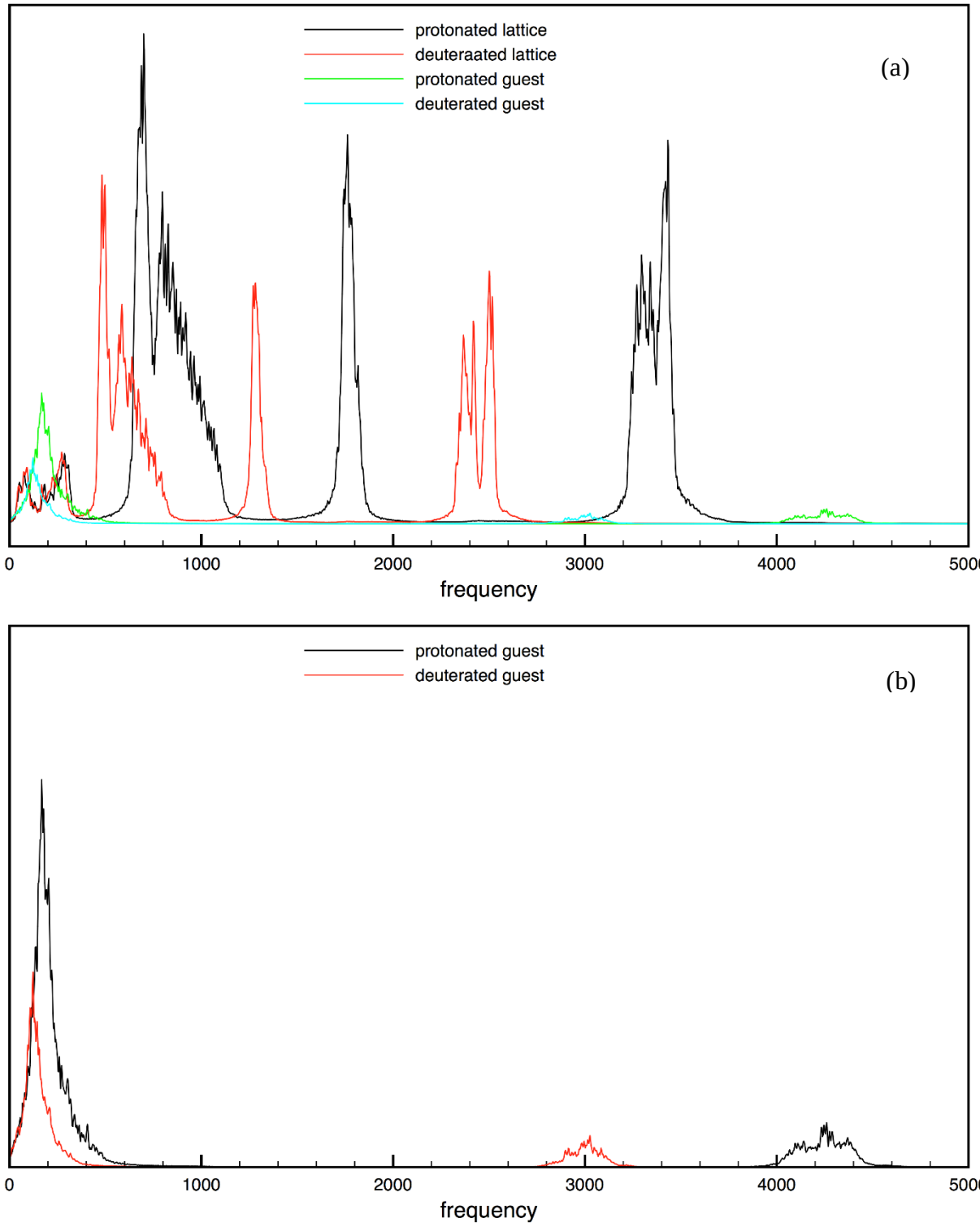

Fig. S2: Full frequency range, up to bond-stretch region, of the (a) lattice and (b) guest proton-velocity spectra.

Temperature dependence of τ_1 and τ_2 bi-exponential times: Arrhenius plots

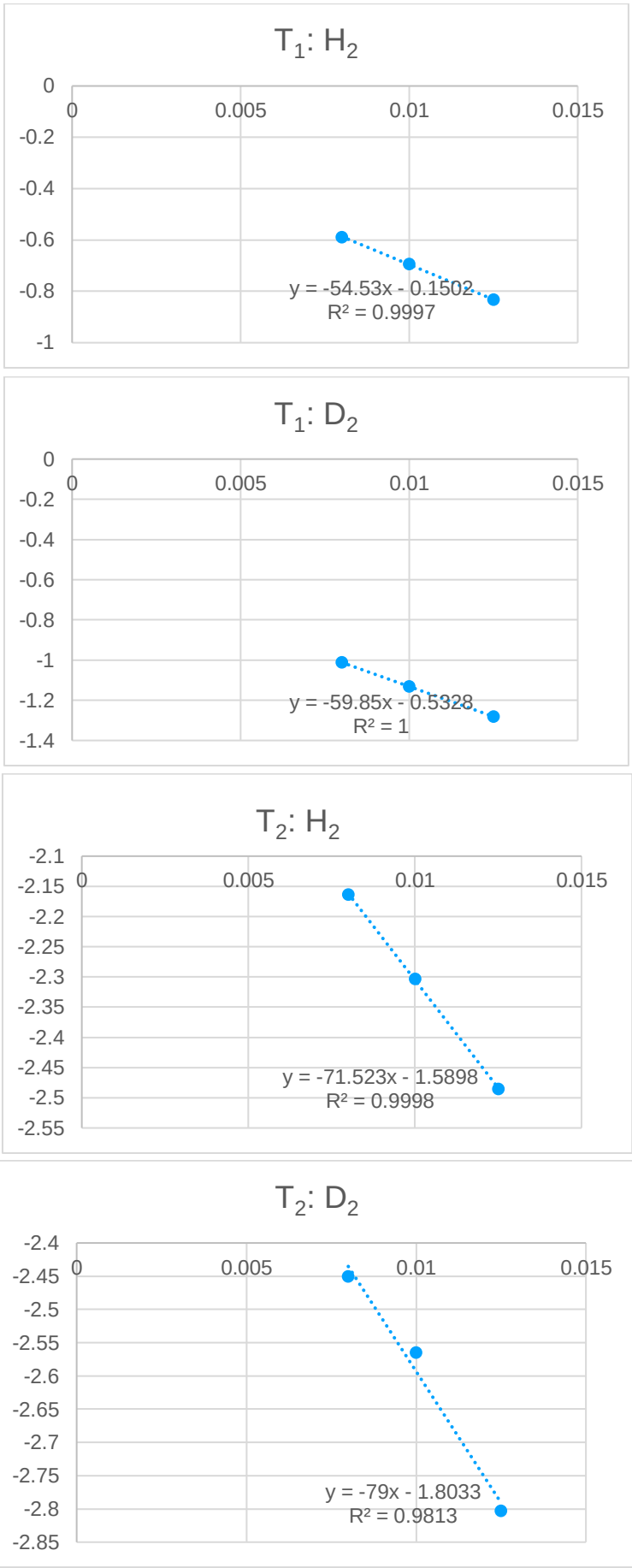

Fig. S3: Arrhenius plots for H_2 and D_2 at 80, 100 and 125 K. Activation energies are: 0.45, 0.50, 0.59, 0.66 kJ/mol for τ_1 (H_2, D_2) and τ_2 (H_2, D_2), respectively.