The Raman signal from a hindered hydrogen rotor

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We study the Raman modes of solid hydrogen and deuterium, testing the assumption that the quantum excitation are localised on one molecule. This is done by direct calculation of the polarisation and explicit solution of the time-dependent Schroedinger equation for an excited, perturbed rotor. Good agreement with experimental results for hydrogen and deuterium support the idea that there are good local quantum numbers in phase I up to 100 GPa, and so the concept of *ortho* and *para* hydrogen remains valid. The rotational energies differ by a factor of 2, which evolves toward $\sqrt{2}$ as the modes acquire librational character due to stronger interactions. The ratio overshoots $\sqrt{2}$ if the anharmonic terms weaken the harmonic potential. We also use density functional theory and molecular dynamics to calculate the $E2_g$ optical phonon frequency and the Raman linewidths, again finding excellent agreement with experiment. Our calculations reveal strong preferred-orientation effects in the experimental sample.