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Efficacious calculation of Raman spectra in high pressure hydrogen

G.J.Ackland^{*,a} and I.B.Magdau^{a1}

¹ ^aCSEC and SUPA, University of Edinburgh, Edinburgh, EH9 3JZ;*

We present and evaluate an efficient method for simulating Raman spectra from molecular dynamics (MD) calculations *without* defining normal modes. We apply the method to high pressure hydrogen in the high-temperature “Phase IV”: a plastic crystal in which the conventional picture of fixed phonon eigenmodes breaks down. Projecting trajectories onto in-phase molecular stretches is shown to be many orders of magnitude faster than polarisability calculations, allowing statistical averaging at high-temperature. The simulations are extended into metastable regimes and identify several regimes associated with symmetry-breaking on different timescales, which are shown to exhibit features in the Raman spectra at the current experimental limit of resolvability. In this paper we have concentrated on the methodology, a fuller description of the structure of Phase IV hydrogen is given in a previous paper¹.

PACS numbers:

I. INTRODUCTION

Hydrogen is the simplest element, yet its high pressure phase diagram is not well established. This is because of the very high pressures at which interesting behaviour occurs, because the structure are highly anharmonic and because crystallography is very challenging. Samples cannot be made of sufficient size to perform neutron scattering at the required pressures, while the X-ray scattering cross-section is weak². Consequently, almost all information about Phase IV comes from spectroscopic experiments^{3,5} and ab initio calculations^{1,6-8}. To make progress we need to be able to compare these data directly to enable a joint experiment/theory attack on the problem, as in our previous work in the related first group elements at pressure⁹⁻¹³.

For a unit cell with N atoms there are exactly $3N$ phonons (i.e. frequencies and eigenmodes) at any wavevector q . The phonons relevant to spectroscopy are those at $\Gamma(q=0)$. The traditional method for spectroscopy simulations is to calculate these phonons, and to understand how they evolve at high temperature. Once the phonons are calculated, Infrared or Raman activity is calculated, thus making the bridge to experiment.

Lattice Dynamics (LD) is the well-established method for phonon calculations based on second derivatives of the energy function. With ab initio methods these can be evaluated either numerically, or by perturbation theory^{14,15}. The phonon spectrum can also be calculated by Fourier transformation of the velocity autocorrelation function calculated by MD. This automatically incorporates anharmonic effects.

Infrared spectra arise from the absorption of energy by a phonon modes which transitions to an excited level. Harmonic oscillations of a particular frequency in the crystal will absorb light at that frequency, leaving gaps in the transmitted light spectrum, provided that the eigenmode is IR active. IR intensity is controlled by the change in the electric dipole moment occurring in a given oscillation mode. The intensity of a transition from state m to state n is given by:

$$I_{nm} \propto \langle m | \mu_a | n \rangle^2 = \sum_a \left(\int \Phi_m^* \mu_a \Phi_n \right)^2; \quad \mu_a = \mu_a^0 + \sum_k \frac{\partial \mu_a}{\partial \epsilon_{ka}} \epsilon_{ka}$$

with a being one of the Cartesian components and the dipole moment μ_a expressed in the basis of the eigenmodes ϵ_{ka} . With orthogonal states Φ_m, Φ_n , the μ_a^0 term does not contribute, so the only contribution to the intensity comes from the change of dipole moment, which can be calculated from the total energy as a linear response¹⁵:

$$\frac{\partial \mu_a}{\partial \epsilon_{ka}} = - \frac{\partial^2 V(r)}{\partial A_a \partial \epsilon_{ka}} = - \frac{\partial F_k}{\partial A_a}$$

where A_a is an external field and F_k are the forces corresponding to each mode k . As such, the IR activity can be calculated using only first order derivatives of the forces.

In the classical picture of Raman spectroscopy, the external field (laser) induces a dipole moment proportional to the polarisability tensor. This induced moment interacts with the field in a second order process: Raman-active phonon eigenmodes does not themselves induce a dipole moment. The intensity depends on third derivatives of the energy¹⁶:

$$P_{kab} \propto \frac{\partial^3 E(r)}{\partial A_a \partial A_b \partial \epsilon_{ka}} = \frac{\partial^2 F_k}{\partial A_a \partial A_b}$$

So matrix elements and cross-terms linking wavefunctions at different k -values must be calculated. This has two important practical effects; Raman intensity calculations are *much* slower than their IR counterparts, and are highly sensitive to k -point sampling. The motivation for the present work is to find proxies for expensive explicit polarisability calculation, so as to devote computing resource to better sampling of the pressure-temperature space.

II. EXTRACTING PHONONS FROM MD

From MD we generate atomic trajectories, $x_i(t)$, at finite temperature. We can expand Cartesian components in terms of the normal modes (ignoring translations).

$$x_j(t) = X_j + \sum_{i=4}^{3N} \alpha_i(t) \epsilon_{ij}; \quad \dot{x}_j(t) = \sum_{i=4}^{3N} \dot{\alpha}_i(t) \epsilon_{ij}$$

This is simply a linear transformation, the normal mode coefficients $\alpha_i(t)$ are fully determined by the Cartesian positions $x_j(t)$. If we assume that we are in the harmonic regime, $\dot{\alpha}_i(t) = \text{Im} [a_i \omega_i \exp^{i(\omega_i t + \phi_i)}]$ with a_i , ω_i and ϕ_i independent of time. This means we can use Fourier Transformed MD data to obtain ω_i . Using the velocity FT is most convenient because anharmonicity may move the mean positions at high temperature, because $\langle \alpha_i \rangle \neq 0$, but $\langle \dot{\alpha}_i \rangle = 0 \forall i$. In the long-time harmonic limit $FT[\dot{\alpha}_i(t)]$ is simply a delta function at $\omega = \omega_i$, in practice we obtain a peak.

This process uses the LD eigenmodes but not the frequencies: finite temperature phonons are calculated from MD, and in the case of strong mixing of LD modes the Fourier transform may show more than one peak. In the harmonic approximation, the same modes will be Raman/IR active in MD and LD. The occupied phonon density of states can be found from the MD velocity autocorrelation function:

$$FT \left[\sum_j \dot{x}_j(t) \dot{x}_j(0) \right] = FT \left[\sum_i \sum_j \dot{\alpha}_i(t) \dot{\alpha}_i(0) \epsilon_{ij}^2 \right]$$

By analogy, the total Raman tensor becomes: $FT \left[\sum_{ij} P_{iab} \dot{\alpha}_i(t) \dot{\alpha}_i(0) \epsilon_{ij}^2 \right]$ and the phonon frequency for each mode i comes from the peak in: $FT [\dot{\alpha}_i(t) \dot{\alpha}_i(0)]$. In the harmonic limit, the Raman signal is simply the sum of individual modes.

Previous methods to obtain high-temperature phonons are based on the idea that the phonon eigenvectors are temperature independent^{17,18}. However, Raman intensities are related to atomic motions, so in the classical approximation they can be extracted directly from linear combinations *without* explicitly evaluating eigenmodes.

For hydrogen the situation is still harder: over the duration of an MD simulation the molecules can rotate, which can totally change the nature of an eigenmode defined by a Cartesian eigenvector (see Fig.1); a method is needed which does not rely on eigenmodes. The key to this is that Raman activity in vibrons comes from in-phase molecular vibrations. For phase III there is only one such mode: all molecules are in similar environments. However in Phase IV the hydrogens in the two layers (B and G, see Fig.2) have very different bond strengths, and consequently do not couple, giving two Raman modes at different frequencies. These are still modes in which all hydrogens vibrate in phase, however the amplitude of vibration is effectively zero in one layer or the other.

This all suggests that rather than projecting onto eigenmodes, we can obtain Raman intensities by projecting the MD trajectories directly onto the in-phase molecular vibration. This requires us to identify molecules at each step of the simulation, which can be done simply by taking shortest bondlengths in almost every case. Our Raman-activity proxy is then: $\alpha_{Raman}(t) = \sum_j [\mathbf{r}_j(\mathbf{t}) - \mathbf{r}_{j_m}(\mathbf{t})]$ where $\mathbf{r}_{j_m}(t)$ is the position of the molecular partner atom to j , at time t . The spectrum for the vibron modes is extracted from velocity autocorrelation of $\alpha_{Raman}(t)$:

$$FT \left[\sum_j \mathbf{v}_j(\mathbf{t}) \cdot [\mathbf{r}_j(\mathbf{t}) - \mathbf{r}_{j_m}(\mathbf{t})] \right]$$

Here we investigate vibrons, but the method is completely general provided that the Raman-active molecular mode can be identified.

III. MOLECULAR DYNAMICS

Molecular hydrogen comprises two indistinguishable protons (fermions) and must have an overall antisymmetric wavefunction. At low pressure it adopts two forms, ortho- and para-, depending on the nuclear spin and rotational

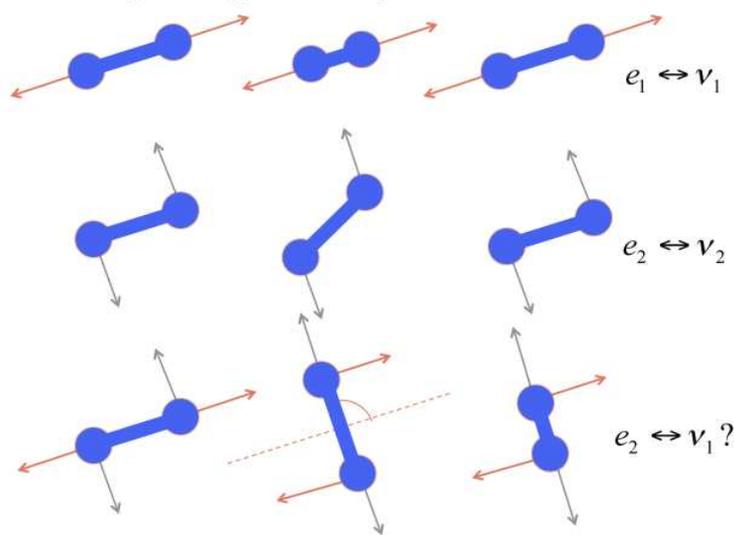


FIG. 1: Failure of projection method for rotating molecule. The upper three images depict a vibron (ν_1), red arrows showing eigenmode and dumbbell showing associated molecular deformation. The central three images show a libron (ν_2 , black arrows). The lower three images show the molecule having rotated through 90 degrees, while the eigenvectors remain fixed in Cartesian coordinates. The red arrows now correspond to the libron, and the black to the vibron. Thus one cannot use normal modes defined in real space for plastic crystals

quantum number J . In phase I, multiple roton bands and a ratio of 2:1 between hydrogen and deuterium roton modes is observed, indicating that these are indeed free rotors and not harmonic oscillators. For vibrons, the ratio close to $\sqrt{2}:1$, showing that these are phonons²¹. Moreover, for Raman frequencies we should consider the excited state of the phonon vibration, whose energy corresponds to several thousand Kelvin, well in excess of the melting point.

All of these effects are neglected both in classical MD²², and the most commonly used alternative, path integral MD, which considers the ground state assuming uncorrelated, distinguishable protons. Nevertheless, the equivalence principle suggests that the vibrations in our calculations should have frequencies corresponding to observation, because the frequency of a harmonic oscillator transition is independent of its quantum number. Although a proper quantum treatment of the proton has not been done here or elsewhere, it is reasonable to assume that the main effect will come from the zero point motion and wavefunction. This in turn will increase the effective displacement of the protons from their equilibrium positions, and although the sampling statistics are different²⁰, to a first approximation it will be equivalent to an increased temperature.

The nature of the phase IV as observed in molecular dynamics is strongly dependent on finite size effects. Small simulations with less than 100 atoms are subject to fluctuations larger than the system size, leading to spurious effects such as layer reconstructions fluctuations between B and G or apparent rapid diffusion. All of our results are taken from simulations of 288 atoms or more.

A stringent test to validate our ansatz and code is provided by considering a randomised hydrogen-deuterium mixture: the different molecular masses on HH, HD, DD break the symmetry and mix all the vibron modes such that they all have some Raman activity. Figure 2 compares results from our proxy with full polarisability calculation^{16,19}. The perturbation theory (DFPT) calculation was done using 1000 processors in 1 week, by contrast the mode projection took 2 minutes on a single processor. Agreement is excellent with slightly more mode-mixing in the MD as one would expect at non-zero temperature. At these low temperatures comparison with a single polarisability calculation is reasonable. At high temperatures the polarisability calculation would need to be done at every MD timestep, and averaged, in order to account for anharmonic temperature effects.

IV. RAMAN RESULTS IN PHASE IV HYDROGEN

Phase IV in hydrogen has been identified as a layered structure (Fig 2) and the vibron spectrum shows one band of frequencies from each layer. We have carried out extensive molecular dynamics using a density functional theory code¹⁹ to describe the electronic structure and classical protons at a range of temperatures and pressures: details were described previously¹.

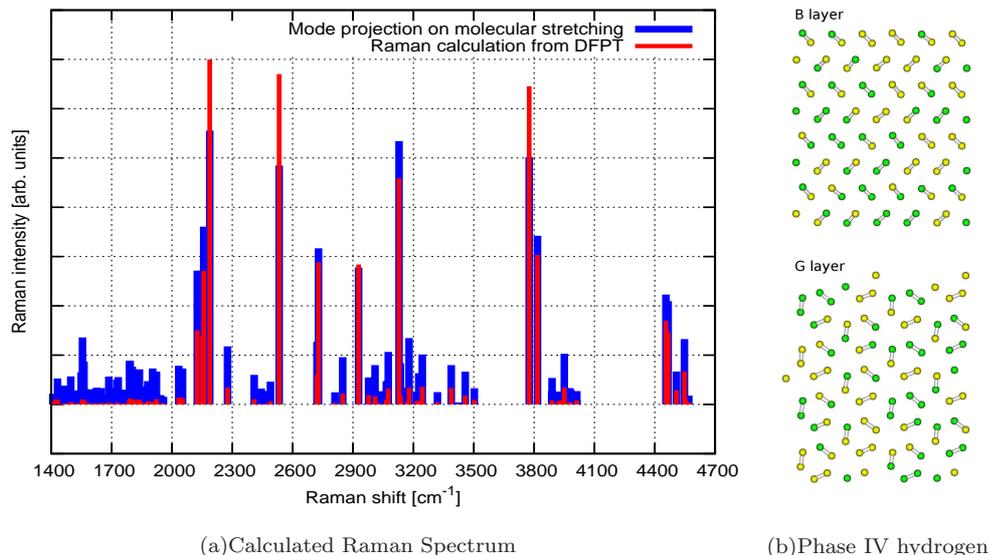


FIG. 2: Comparison of calculated Raman vibron intensities using polarisability from third-order wavefunction derivatives (red) and projection from molecular dynamics (blue) for Phase IV with randomly placed H-D isotopes, within the Pc structure^{1,6,7} which has alternating molecular (B) and trimer (G) layers.

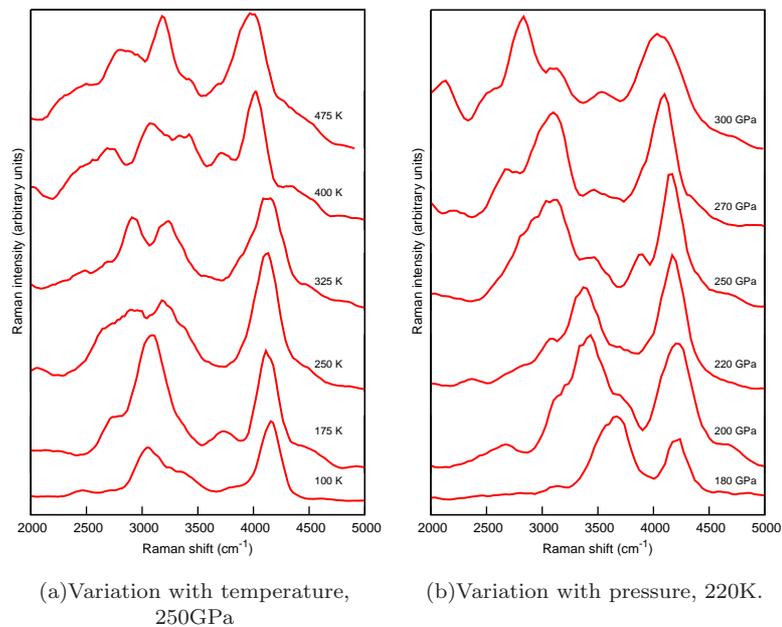


FIG. 3: Calculated Raman signals from ab initio runs using CASTEP. Simulations were equilibrated in Phase IV, then averages taken over 3000 steps NVE pure H₂, 288 atoms

Fig 3 shows the variation with temperature and pressure. The pressure evolution has been studied experimentally, and the main features are all well reproduced by the calculation: there are two strong peaks - indicating strongly bonded B layer and weakly bonded G layer; There are sharp peaks in the B layer - indicating weak coupling and low anharmonicity; There are broad peaks in the G layer - indicating stronger intermolecular interactions which weaken the intramolecular bonds and increasing anharmonicity with pressure; there is a shoulder on the G-layer peak - indicating the high pressure onset of trimer rotation.

Temperature trends are less well studied experimentally, but from the simulations we predict two trends which

should be measurable: Softening of the B layer peak with increasing T; Broadening and splitting of the G - layer peaks.

It is important to note that the simulation extend far beyond the thermodynamic stability range of Phase IV. We have seen evidence of spontaneous III-IV phase transitions in the MD, however this is strongly suppressed by the finite system size.

V. CONCLUSIONS

We have show that high temperature Raman data can be extracted from molecular dynamics simulations without recourse to polarisability calculations. The projection method has been used widely before^{17,18} for highly symmetric crystals where the eigenmodes are determined by symmetry and the anharmonicity can be used to renormalise their frequencies. For hydrogen, where the normal modes themselves have only temporary validity, we have to extract the signal without recourse to normal modes. The basis of the method is the ansatz that the Raman signal can be associated directly with molecular motions (symmetric vibrons) and therefore calculated *without* explicit evaluation of phonon modes. It must be admitted that the method is more challenging with respect to IR modes, which are related to out-of-phase vibrations: these are non-unique in a crystal with a large basis such as Phase IV hydrogen. However, some information can still be extracted from another ansatz - that the IR active modes are drawn from the high frequency end of each band and are of similar width to the Raman.

* *Corresponding author. Email: gjackland@ed.ac.uk

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- ²¹ In fact, experimental H:D frequency ratios for vibrons are slightly lower than $\sqrt{2}$:1 in Phase IV, indicating that rotation is hindered and the potential is slightly stiffer than harmonic.
- ²² We did investigate placing large a energy in the vibron eigenmode and monitoring its decay. This showed that the B-layer modes are longer-lived and the peaks should be sharper, but did not give quantative results.