Rapid Quantum Tunnelling in *my* NnVH Defects? It's More Likely Than You Think.

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NnVH Defects in Diamond

- NnVH defects in diamond are made up of n substitutional **N**itrogens, where $n \in \mathbb{Z} \cap [0, 3]$, surrounding a **V**acancy, with a **H**ydrogen sitting in the vacancy.
- EPR experiments observe high point group symmetry for this defect family when $n \neq 3$, leading to the assumption that the hydrogen is sitting in the centre of the vacancy.
- Ab initio studies disproved this, showing that the hydrogen is much too unstable. This lead to the theory that the hydrogen is in fact *rapidly* reorienting between equivalent carbon sites surrounding the vacancy, giving rise to an averaged higher order symmetry under EPR.
- Classical estimations for the reorientation rate give much too low values for this to be the case, so the hydrogen must be quantum tunnelling between sites!

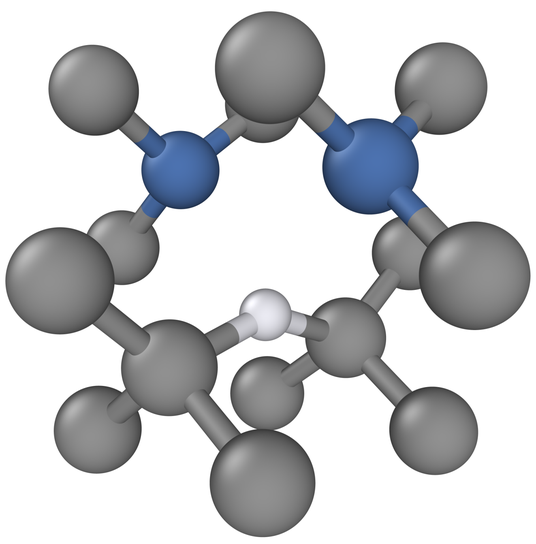

Figure 1. N_2VH in its averaged C_{2v} symmetry position, switching rapidly between the two central carbons. Hydrogen is shown in white, nitrogen in blue, and carbon in grey, most of the surrounding structure has been omitted for clarity. Generated using OVITO.

Attempt Frequency from Phonon Modes

- In order to calculator the tunnelling rate, Γ, the attempt frequency, k, acting on the barrier must be known.
- A **finite displacement** calculation was performed on N_2VH to get a $3N \times 3N$ *dynamical matrix* that contains the force created on all N atoms due to the displacement of each atom from its origin.
- This can also be represented as the second derivative of energy with respective to atomic displacements, r, of atoms i and j.

$$\frac{\mathrm{d}^2 E}{\mathrm{d}r_i \, \mathrm{d}r_j} \frac{1}{\sqrt{m_i \, m_j}}$$

- This can be solved to retrieve the wavenumbers of the phonon modes, k, and their directions on each atom, i, ν_{ik}
- The frequency at which the hydrogen vibrates can be approximated to be the attempt frequency, k. This can be found by finding the strength of each phonon mode of hydrogen acting in the direction of tunnelling.

$$k = \sum_{k}^{3N} \vec{\nu}_{Hk} \cdot \vec{r}_H = 40.872\,\mathrm{THz} = 1363\,\mathrm{cm}^{-1}$$

- This is very close to the one-phonon mode of diamond, $1332\mathrm{cm}^{-1}$, which has previously been used as an estimation for these calculations, justifying its further use here.

Computational Details

- All calculations were performed using CASTEP 23.1, using a periodic 64 atom simulation cell.
- The meta-GGA RSCAN functional was used for all calculations unless stated otherwise.
- A plane wave cut-off of $1\,000$ eV and a $4 \times 4 \times 4$ Monkhorst-Pack k-point grid was used, with a force tolerance of 0.02 eV / Å for geometrical minimisation.
- A lattice constant of 3.5537 was found during convergence testing, close to the experimental value of 3.567.

Tunnel 'er? I hardly know 'er!

- The **WKB Approximation** is used to calculate the probability, P, of tunnelling through the potential energy barrier.
- The integral is performed between the *turning points* of the energy barrier, a and b, where the potential energy, $V(q)$ and kinetic energy, $E(T)$ of the system are equal, such that $V(q) = E(T)$.

$$P = \exp\left(\frac{-4\pi}{h} \int_a^b \sqrt{2\mu \left(V(q) - E(T)\right)}\, \mathrm{d}q\right)$$

- Where μ is the reduced mass of the system, h is Planck's constant, and q is the reaction coordinate/minimum energy path.

Coupling Constant

It is not *only* the hydrogen that moves when quantum tunnelling is taking place, the atoms neighbouring the vacancy also account for a small amount of the total reaction coordinate.

We can consider a coupling constant, c_i for each atom i, which details how strongly its motion is coupled to the reaction coordinate. Where u_i is the cumulative displacement, and Q is the total displacement covered by the path.

$$c_i = \left(\frac{u_i}{Q}\right)^2$$

Therefore when calculating the reduced mass, μ we consider each atom in proportion to its coupling constant.

$$\frac{1}{\mu} = \sum_i \frac{1}{m_i} c_i$$

Energy Levels

- Although anharmonic effects are most likely present, the motion of the atoms can approximated as a quantum harmonic oscillators (QHO), with phonon modes either aiding and obstructing to motion along the reaction coordinate, meaning each phonon mode ν_i is actually a one-dimensional vector quantity. For the ground state approximation, we can find the vibrational frequency
- With the phonon modes pointing in the direction of the reaction coordinate already, we can find the energy of a certain atom as

$$E(\nu, T) = h\nu \left(\frac{1}{2} + n(\nu, T)\right)$$

- Where is the $n(\nu, T)$ Bose-Einstein distribution, used here to find how occupied each phonon mode is at a certain temperature.

$$n(\nu, T) = \frac{1}{e^{h\nu / kBT} - 1}$$

- All of these energies can then be summed to get the energy of the oscillations of an atom along the reaction coordinate. Where k specifies a certain phonon mode.

$$E_i(T) = \sum_k E(\nu_k, T)$$

- Then when calculating the total energy, we can once again scale by the coupling index c_i

$$E(T) = \sum_i E_i(T)\, c_i$$

WTF IS NnVH?? WHY IS IT COOL? HERE'S WHY

To Tunnel or not to Tunnel

Previous studies have calculated the ab initio energy barrier for every viable NnVH defect, however they have not used those results to fully calculate the reorientation rate of the Hydrogen when possible. The full calculation of reorientation rate for each defect is shown, many of these defects have yet to be observed in experiment.

Defect		Barrier / eV	Rate / GHz 0 K	100 K	300 K
VH^0	$S = 3/2$	0.378	0		
VH^-	$S = 1$	0.707	0		
VH^+	$S = 0$	0.995	0		
NVH^0	$S = 0$	0.926	0		
NVH^0	$S = 1$	0.572	0		
NVH^-	$S = 1/2$	0.410	0		
NVH^+	$S = 1/2$	0.607	0		
N_2VH^0	$S = 1/2$	0.677	0		
N_2VH^-	$S = 0$	0.157	0		
N_2VH^+	$S = 0$	0.613	0		

Table 1. Comparison of the different quantum tunnelling energy barriers for different NnVH defects in diamond, along with their comparison to previous ab initio studies. The rates at two different temperatures are calculated for each defect with the methods previously shown.

Nudged Elastic Band (NEB)

- Computational method to find the minimum energy path (MEP) between two different states, in this case a hydrogen atom moving between two equivalent carbons.
- Evenly spaced interpolated images are generated between the two states, connected by virtual springs, so that the forces between each image keep them evenly spaced.
- This method will give us an energy barrier along the minimum energy path, also known as the reaction coordinate, which can then be used to calculate the quantum tunnelling rate.
- **Gaussian Process Regression** can be used to interpolate along the path, no one is actually going to read this, giving an estimated function for a continuous path which can then be integrated over.

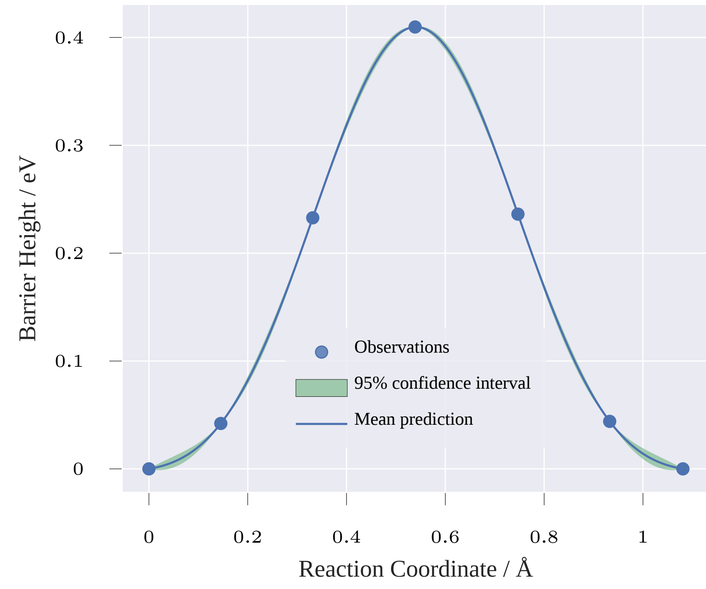

Figure 2. The NEB plot of the NVH^0 $S{=}\frac{1}{2}$ defect, showing the cumulative displacement of the minimum energy path on the x-axis, and the potential energy, or barrier height, on the y-axis. The shape is typical of every NnVH defect.

References

[1] Claude E. Shannon. A mathematical theory of communication. *Bell System Technical Journal*, 27(3):379–423, 1948.