An ultrafast shakedown reveals the energy landscape, relaxation dynamics and concentration of hydrogen related modes in diamond

D. J. L . Coxon[1,2,3*], M. Staniforth[1,2], J. Lloyd-Hughes[1], V. G. Stavros[2], M. E. Newton[1]

[1] Department of Physics, University of Warwick, Coventry, UK, CV4 7AL
[2] Department of Chemistry, University of Warwick, Coventry, UK, CV4 7AL
[3] EPSRC Centre for Doctoral Training in Diamond Science and Technology, UK
* D.J.L.Coxon@warwick.ac.uk

Atomic-scale defects can control the exploitable optoelectronic performance of crystalline materials, and several point defects in diamond are emerging functional components for a range of quantum technologies. Nitrogen and hydrogen are common impurities found in diamond, and there is a family of defects that incorporates both.

The N_3VH^0 defect is a lattice vacancy where three nearest neighbour carbon atoms are replaced with nitrogen atoms and a hydrogen is bonded to the remaining carbon. It is regularly observed in natural and high-temperature annealed synthetic diamond and gives rise to prominent absorption features in the mid-infrared, with the most intense of these being found at a wavenumber of 3107 cm^{-1}. Many other features in the infrared were discovered alongside the 3107 cm^{-1} feature and have since also been attributed to N_3VH^0. [1,2]

However, the defect responsible for the sharp infrared feature at 3237 cm^{-1} has not been identified. This feature has been found in many type Ia and Ib natural diamonds, and in some HPHT diamonds. In each case, it does not correlate with the N_3VH^0 group of features, though it is often seen together with them. De Weerdt *et al.* found no ^{13}C isotopic shift in the 3237 cm^{-1} feature during their studies on HPHT samples. [3] They proposed it to originate from an N–H stretch mode and suggested an amide group as the defect. However, no carbonyl stretch has been located in FTIRs containing this feature, so this assignment is uncertain.

Here, we combine time- and spectrally resolved infrared absorption spectroscopy to yield unprecedented insight into the N_3VH^0 defect's vibrational dynamics following infrared excitation of the C−H stretch. In doing so, we gain fundamental information about the energies of quantized vibrational states and corroborate our results with theory. We map out, for the first time, energy relaxation pathways, which include multiphonon relaxation processes and anharmonic coupling to the C−H bend mode. We carry out a similar investigation on the unknown defect corresponding to the 3237 cm^{-1} feature, observing different dynamics which appear to be sample-dependent, unlike those of N_3VH^0. These advances provide new routes to quantify and probe atomic-scale defects and may offer a new route to their identification.

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