

A Density Functional Theory Study on the Point Defects in PuO₂

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Vibrational spectroscopy, particularly Raman, is an important technique when applied to plutonium dioxide (PuO₂), as it can provide valuable insights into a given sample ageing history as radiation defects develop over time. To underpin this spectroscopic feature of PuO₂, we are simulating vibrational spectra of PuO₂ containing defects.

Factor group analysis of the space group of PuO₂ (Fm $\bar{3}$ m, face-centred cubic; O_h^5 point group) predicts the observation of one Raman active phonon (T_{2g}), experimentally observed at ~480 cm⁻¹, however alpha decay and formation of defects can cause the T_{2g} band to appear at lower wavenumbers, broaden and decrease in intensity. Radiation damage in PuO₂ generates new peaks in the Raman spectrum, such as those seen in the experimental literature in the 530-660 cm⁻¹ region, attributed to the formation of various defects. These include various point defects, anionic Frenkel pairs, cationic Frenkel pairs and alpha helium. The Raman-inactive mode (1LO2) is thought to become Raman active through symmetry lowering and lattice disorder and appears in the region ~580 cm⁻¹, possibly following the formation of Frenkel oxygen defects generated through alpha decay.

Computational modelling of this subject provides a more fundamental understanding of the self-irradiated PuO₂ Raman spectra. This study employs Density Functional Theory including spin orbit interaction to investigate the vibrational fingerprint of pure and defective PuO₂, focusing on the IR and Raman signatures. The defects investigated in this study are various point defects, due to their relevance in the experimental literature.