[MS20-P15] Dependency of oscillation frequencies of crystalline materials on changing pressure conditions; experimental study vs. theoretical calculations

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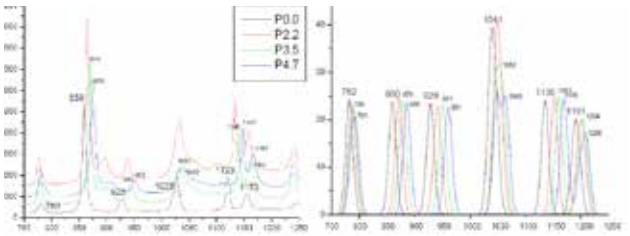
We studied dependency of oscillation frequencies of crystalline materials on changing pressure conditions and checked to what extent periodic boundary calculations are able to reproduce this effect. L-Alanine, DL –Alanine and α – Glicyne crystal structures were chosen for the study, mainly because a sufficient number of results from high pressure X-ray and spectroscopic measurements is available for them. [1], [2]. For each crystal structure, series of periodic boundary theoretical calculations were performed with different constrains. In these calculations, unit cell parameters were constrained to the values obtained from the X-ray measurements performed in given pressure conditions (from ambient pressure to 6GPa). For ambient pressure, consistence of theoretical calculations performed with several basis sets and levels of theory were checked with respect to experimental results. Finally, DFT method with Grimme dispersion correction [4] modified as proposed by Civalleri [5] and cc-pVTZ basis set were chosen for the current study. Afterwards, on the bases of the calculations theoretical Raman and IR spectrums were obtained for all the studied crystal structures and given pressure conditions. Spectrums obtained theoretically were compared to experimental Raman and IR results collected in corresponding pressure conditions. The theoretical spectrums were also compared to the results of theoretical calculations performed without constrains of unit cell parameters.
At the end, crystal structures obtained from X-ray measurements performed in different pressure conditions andrerefined using TAAM [6] model were compared to the crystal structures optimized in the periodic boundary theoretical calcula For ambient pressure, consistence of theoretical calculations performed with several basis sets and level of theory were checked with respect to experimental results. Finally, all the theoretical calculations were performed using DFT method with Grimme dispersion correction [4] modified as proposed by Civalleri [5] and cc-pVTZ basis set. Afterwards, on the bases of the calculations theoretical Raman and IR spectrums were obtained for all the studied crystal structures and given pressure conditions. Spectrums obtained theoretically were compared to experimental Raman and IR results collected in corresponding pressure conditions.tions where corresponding unit cell parameters were constrained. With increasing pressure, we observed shifts of oscillation frequencies to the higher values. The oscillation frequency values lower than 1500 cm^{-1}, as well as their shifts caused by changing pressure conditions, were well predicted by periodic boundary calculations performed with constrained unit cell parameters. For higher energy modes some scaling was necessary.



(a) (b)

Figure 1. (a) Experimental (b) theoretical Raman spectrum of L-Alanine crystal structure estimated/collected in subsequent pressure conditions: ambient, 2.2 GPa, 3.5 GPa, 4.7 GPa.

[1] data collected by Tumanow, N. & Boldyreva
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