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First-Principles Study of Phonon Anharmonicity in Atomically-Thin Black Phosphorus

Black phosphorus (BP) consists of anisotropic puckered layers held together by long-range van der Waals forces, which allows for the isolation of single-layers [1]. This material is of interest due to its semiconducting band gap which remains direct independent of the number of layers [2], as well as its high carrier mobility [3]. It was shown experimentally that the Raman active modes A_g^1, B_{2g}, and A_g^2 have frequencies which downshift with increasing temperature [4]. In this work we study this phenomenon for the single-layer using first-principles density functional theory (DFT) calculations. To model the temperature-induced shift of the phonon frequencies, we carry out *ab initio* molecular dynamics simulations with varied temperature. The normal mode frequencies are located at the peak positions in the power spectrum, which is calculated as the magnitude of the Fourier transform of the total velocity autocorrelation. We extend this approach to anharmonic systems by approximating the general solution to the classical equations of motion as a superposition of normal modes, with each mode written as a Fourier series. Anharmonicity induces a frequency shift for each mode individually as well as from phonon-phonon coupling, with the latter interpreted classically as an effective damping of a given mode due to its interaction with all other modes. The effect of thermal expansion is also included by imposing the temperature dependent lattice constant in each simulation as calculated within the quasiharmonic approximation. In general we obtain frequency downshifts with increasing temperature in agreement with experiment, with the results visualized in Figure 1.

References

[1] H. Liu *et al.*, ACS Nano, 8 (2014) 4033
[2] L. Li *et al.*, Nature Nanotechnology, 12 (2017) 21
[3] G. Long *et al.*, Nano Letters, 16 (2016) 7768
[4] A. Łapińska *et al.*, The Journal of Physical Chemistry C, 120 (2016) 5265

Figures

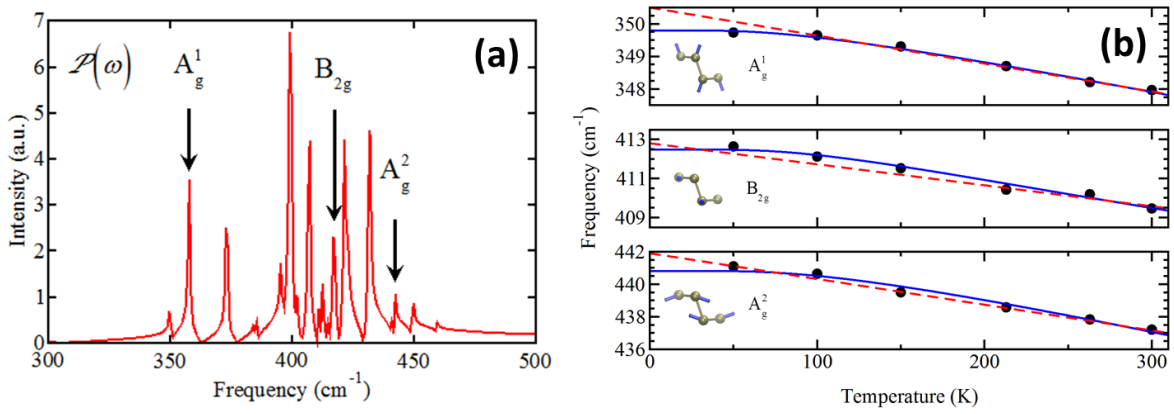

Figure 1: (a) Sample power spectrum with the Raman active mode peaks identified. (b) Predicted frequency shifts with varied temperature.