Temperature-dependent asymmetric shapes of Raman bands in transition metal dichalcogenides and their heterostructures

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By using first-principles DFT modeling and a rigorous theoretical approach to calculating first-order Raman scattering cross-sections [1], we study temperature-dependent shapes of Raman bands in popular representative van der Waals materials [2]: including 2*H*-MoS_2, a heterostructure of 2*H*-MoS_2/graphene, and semi-metallic 1*T*-TiS_2. We consider anharmonicity-induced effects in the models: thermal expansion and all significant phonon-phonon scattering processes.

While it is well-known that the anharmonicity of a crystal typically causes a red-shift of Raman bands' positions and broadens their linewidths, it is usually not taken into account that anharmonicity-induced changes are internally dependent on Raman shift of the incident light [1]. Consequently, the shapes of observed Raman bands might not remain perfectly Lorentzian. Instead, they can take the form of quasi-Lorentzian functions with centers and broadening parameters dependent on Raman shift, leading to an asymmetry of the Raman bands [1].

In our work, we comprehensively study positions, bandwidths, and asymmetry of Raman bands in the above-listed van der Waals materials. The parameters of each band are dominated by the anharmonicity of the system, which itself increases with the temperature. The most intriguing and counter-intuitive situation occurs in 1*T*-TiS_2, in which large anharmonicity leads to a significant dependence of the first-order A_{1g} band's parameters on Raman shift and to its asymmetric broadening – making an illusion of another band's formation.

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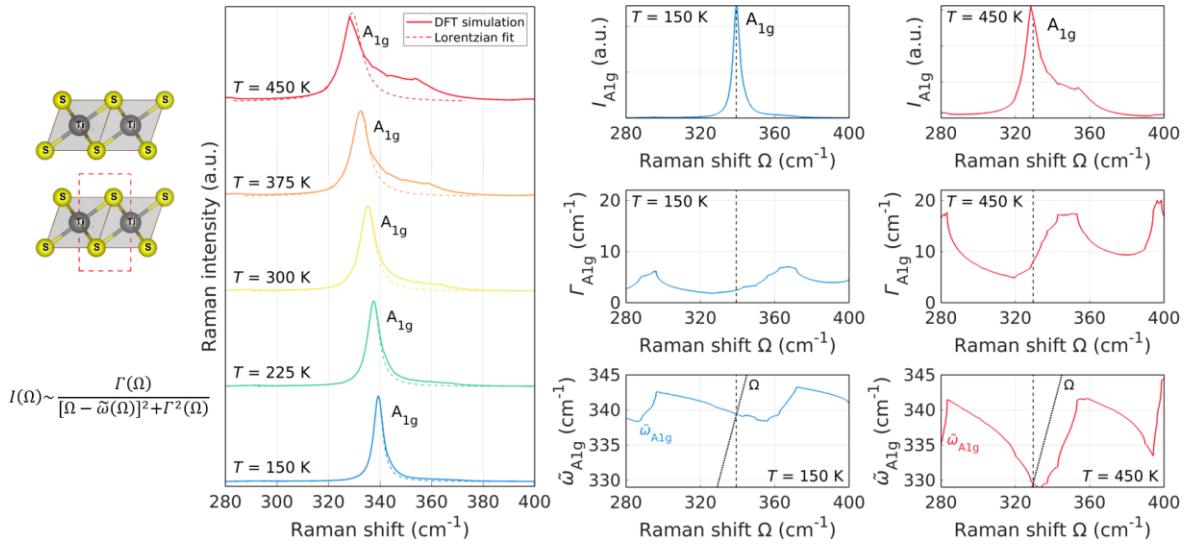

Fig. 1. Temperature evolution of the A_{1g} Raman band in TiS_2 and dispersion of its quasi-Lorentzian parameters.

[1] R. A. Cowley, Rep. Prog. Phys., **31**, 123 (1968).
[2] X. Yan *et al.*, Sci. China Phys. Mech. Astron., **65**, 117004 (2022).