

Resonant multiphonon Raman scattering in MoS₂ up to the fifth order

Tsachi Livneh^{1*} and Jonathan E. Spanier²

¹ Department of Physics, NRCN, P.O. Box 9001, Beer-Sheva, 84190, Israel.

² Department of Materials Science & Engineering, Drexel University, 3141 Chestnut St., Philadelphia, PA, 19104, USA.

T.Livneh@nrcn.org.il

We present a comprehensive multiphonon Raman analysis for bulk and monolayer MoS₂ [1]. For the bulk, the analysis consists of symmetry assignment from which we obtain a broad set of allowed second-order transitions at the high symmetry M, K and Γ Brillouin zone (BZ) points. We assign about 100 transitions of up to fifth-order processes in the low temperature resonant Raman spectrum measured with excitation energy of 1.96 eV, which is slightly shifted in energy from the A exciton. The main contributions come from four phonons: A_{1g} (M), E¹_{2g} (M₂), E²_{2g} (M₁) (TA' (M)) and E²_{2g} (M₂) (LA' (M)). The last three are single degenerate phonons at M with an origin of the E¹_{2g} (Γ) and E²_{2g} (Γ) phonons -see the acoustic phonon branches in the vicinity of M and K points, presented in Fig. 1A [2].

Due to fact that at the M-point only combinations with the same inversion symmetry (*g* or *u*) are Raman-allowed, the contribution of combinations with the LA (M) mode are not expected with the above four phonons. Although minor, contributions from K-point and possibly Γ -point phonons are also evident.

Among the four "resonant group" phonons, we identify in the resonant Raman spectra all of the second-order overtones, combination and difference-bands and many of the higher-order bands. An extension (up to ~1530 cm⁻¹) of a recently presented [1] low temperature spectrum is shown in Fig. 1B. A set of calculated frequencies of multiphonon transitions, of all the possible combination bands (within the presented spectral range and up to the forth-order) of n₁*E¹_{2g} (M₂)+ n₂*A_{1g} (M)+ n₃*TA' (M) + n₄*LA' (M), with n₁,n₂=0-3, n₃,n₄=0-2, is depicted with blue bars. They are also presented in the attached table (the 5LA'(M) band is also shown for completeness).

The validation of this multiphonon scheme for 2H-MoS₂ is substantiated by the excellent agreement between the predicted and measured frequencies and its distinctive capability to be employed throughout the full spectral range for difference-bands, combination-bands and overtones [1].

[1] T. Livneh and J.E. Spanier, *2D Materials* **2** (2015), 035003.

[2] C. Ataca, M. Topsakal, E. Akt, and S. Ciraci, *J. Phys. Chem. C* **115**, (2011), 16354.

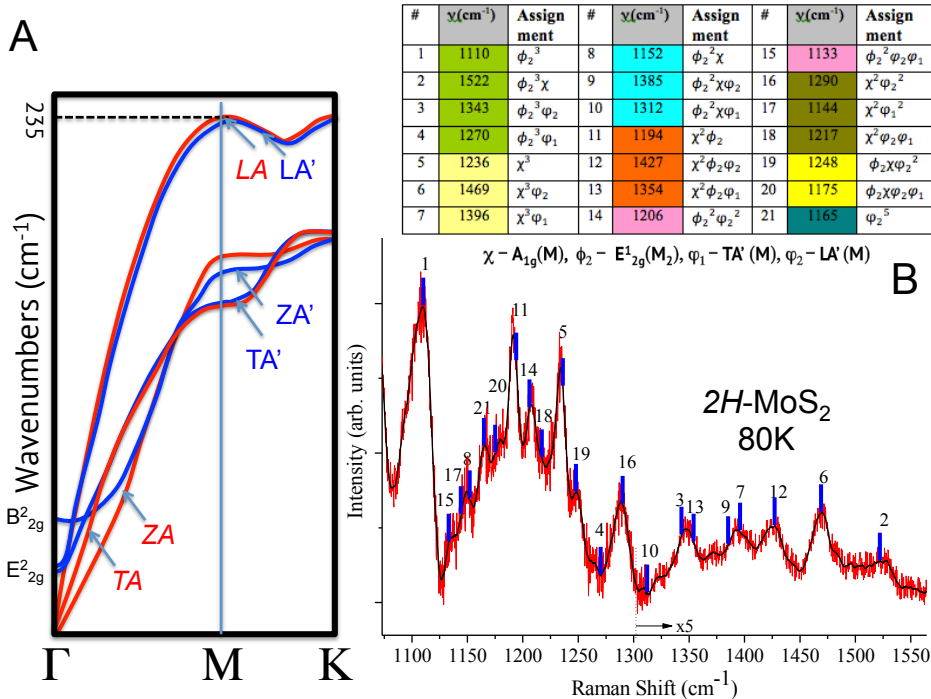


Figure 1