Resonant multiphonon Raman scattering in MoS_2 up to the fifth order

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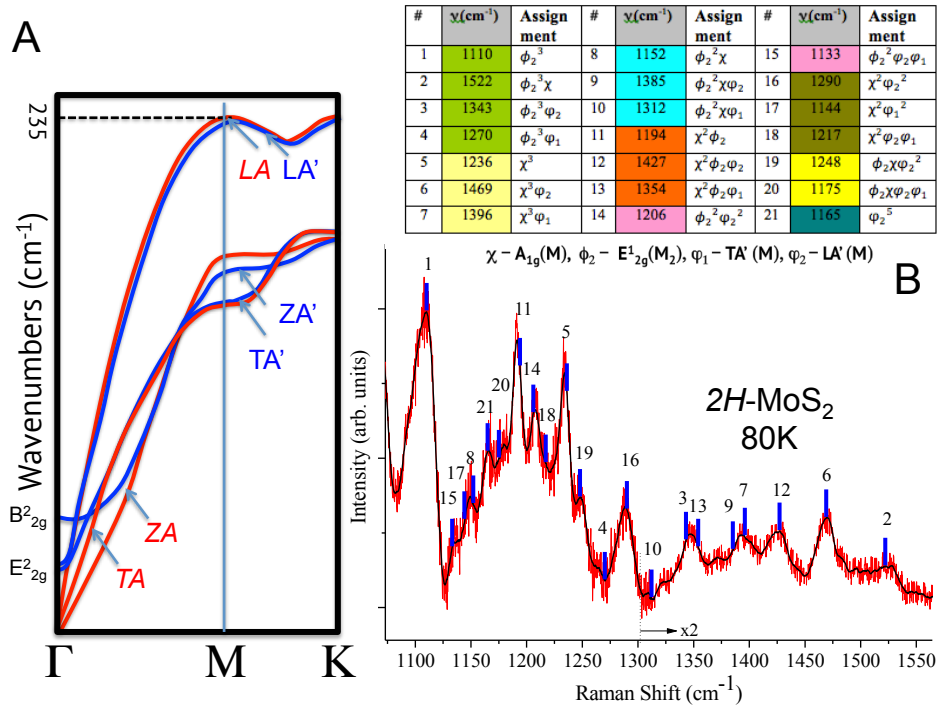
We present a comprehensive multiphonon Raman analysis for bulk and monolayer MoS_2 [1]. For the bulk, the analysis consists of symmetry assignment from which we obtain a broad set of allowed second-order transitions at the high symmetry M, K and Γ Brillouin zone (BZ) points. We assign about 100 transitions 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), E^1_{2g} (M_2), E^2_{2g} (M_1) (TA' (M)) and E^2_{2g} (M_2) (LA' (M)). The last three are single degenerate phonons at M with an origin of the E^1_{2g} (Γ) and E^2_{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*E^1_{2g} (M_2)+ 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*-MoS_2 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.



#	ν(cm⁻¹)	Assignment	#	ν(cm⁻¹)	Assignment	#	ν(cm⁻¹)	Assignment
1	1110	ϕ_2^3	8	1152	$\phi_2^2\chi$	15	1133	$\phi_2^2\varphi_2\varphi_1$
2	1522	$\phi_2^3\chi$	9	1385	$\phi_2^2\chi\varphi_2$	16	1290	$\chi^2\varphi_2^2$
3	1343	$\phi_2^3\varphi_2$	10	1312	$\phi_2^2\chi\varphi_1$	17	1144	$\chi^2\varphi_1^2$
4	1270	$\phi_2^3\varphi_1$	11	1194	$\chi^2\phi_2$	18	1217	$\chi^2\varphi_2\varphi_1$
5	1236	χ^3	12	1427	$\chi^2\phi_2\varphi_2$	19	1248	$\phi_2\chi\varphi_2^2$
6	1469	$\chi^3\varphi_2$	13	1354	$\chi^2\phi_2\varphi_1$	20	1175	$\phi_2\chi\varphi_2\varphi_1$
7	1396	$\chi^3\varphi_1$	14	1206	$\phi_2^2\varphi_2^2$	21	1165	φ_2^5

Figure 1