A comprehensive multiphonon spectral analysis in MoS$_2$

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Abstract

We present a comprehensive multiphonon Raman and complementary infrared analysis for bulk and monolayer MoS$_2$. 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 $\Gamma$ Brillouin zone (BZ) points. The attribution of about 80 transitions of up to fifth order processes are proposed in the low temperature (95 K) resonant Raman spectrum measured with excitation energy of 1.96 eV, which is slightly shifted in energy from the $A_{\text{exciton}}$. We propose that the main contributions come from four phonons: $A_{1g} (M)$, $E_{12g} (M_1)$, $E_{2g} (M_1)$ ($TA' (M)$) and $E_{2g} (M_2)$ ($LA' (M)$). The last three are single degenerate phonons at M with an origin of the $E_{12g} (\Gamma)$ and $E_{2g} (\Gamma)$ phonons. Among the four phonons, we identify in the resonant Raman spectra all (but one) of the second-order overtones, combination and difference-bands and many of the third order bands. Consistent with the expectation that at the M point only combinations with the same inversion symmetry (g or u) are Raman-allowed, the contribution of combinations with the longitudinal acoustic (LA(M)) mode can not be considered with the above four phonons. Although minor, contributions from K point and possibly $\Gamma$-point phonons are also evident. The ‘2LA band’, measured at $\sim 460$ cm$^{-1}$ is reassigned. Supported by the striking similarity between this band, measured under off-resonant conditions, and recently published two phonon density of states, we explain the lower part of the band, previously attributed to 2LA(M), as being due to a van Hove singularity between K and M. The higher part, previously attributed exclusively to the $A_{2u} (\Gamma)$ phonon, is mostly due to the LA and LA’ phonons at M. For the monolayer MoS$_2$ the second-order phonon processes from the M and $\Gamma$ BZ points are also analyzed and are discussed within similar framework to that of the bulk.

1. Introduction

Recently, Raman scattering has been increasingly important in the study of transition-metal-layered-type-dichalcogenides [1–16]. Among those, the most investigated system is the indirect semiconductor MoS$_2$, with the $2H$ hexagonal polytype (D$_{6h}$ space group #194), which becomes a direct band-gap semiconductor in monolayer $1H$ polytype [16]. Raman scattering was employed for the various forms of bulk [1–6], inorganic fullerenes (IF) [7] and few layer (FL) structures down to the monolayer [8–13]. A group-theoretical analysis of the optical lattice vibrations for the bulk [1] reveals four Raman-active modes corresponding to the following symmetries with measured frequencies under ambient conditions: $E_{2g}^i$ (35 cm$^{-1}$), $E_{1g}$ (286 cm$^{-1}$), $E_{2g}^l$ (383 cm$^{-1}$), and $A_{1g}$ (408 cm$^{-1}$). In addition, there are two IR-active modes: $E_{1u}$ (384 cm$^{-1}$), $A_{2u}$ (470 cm$^{-1}$), and four silent modes: $B_{2g}^i$ (58 cm$^{-1}$) [11], $E_{2u}$ (287 cm$^{-1}$), $B_{1u}$ (403 cm$^{-1}$) and $B_{2g}^l$ ($\sim 475$ cm$^{-1}$). In addition to observation of first-order Raman lines these and other studies showed a rich multiphonon spectrum [2, 3, 6, 7, 9, 10, 13–15] with sensitivity to excitation energy [6, 7, 9, 10, 13].

The higher order spectra of bulk MoS$_2$ have been assigned [2, 3] to be mostly constructed from second-order transitions (some of which include the...
longitudinal acoustic (LA) phonon at the M Brillouin zone (BZ) edge, LA(M), and BZ center $\Gamma$-point phonons. Stacy and Hodul [3] focused on the nature of the band around $\sim 465$ cm$^{-1}$, which is denoted hereafter as the ‘2LA band’ and assigned it to a second-order process involving the LA(M) phonon. Frey et al [7] studied this band for IF and bulk MoS$_2$, suggesting that the asymmetric features of 2LA band are due to a combination of two peaks centered at room temperature at $\sim 454$ cm$^{-1}$ (denoted here as $\alpha_1$) and $\sim 465$ cm$^{-1}$ ($\alpha_2$). The first is assigned to the 2LA(M) and the second to a Raman-forbidden IR-allowed optical $A_{\text{g}}(\Gamma)$ mode, which involves asymmetric translation of both Mo and S atoms parallel to the $c$ axis [1]. It was argued that, although not allowed by Raman selection rules, under resonance conditions excitons could mediate the scattering of this phonon. The above assignment of the ‘2LA band’ has been adopted exclusively in the literature [6–15].

Although the K-point phonons may also contribute, it was proposed that due to the fact that the 2LA(K) frequency was found (according to [17]) to be higher by $\sim 10$ cm$^{-1}$ at the K point relative to the M point, their contribution is minor. This was in contrast to 2H-WS$_2$, which was argued by Sourisseau et al [17] to have a multiphonon spectrum mostly constructed from combination and difference bands with LA phonons at the K point.

Here we present a comprehensive multiphonon analysis in bulk 2H-MoS$_2$. Supported by new evidence, we propose modified interpretations and assignments of some of the central spectral features. Significantly, our findings challenge the widely accepted one [3] according to which the majority of the observed second-order combination and difference bands from the M point are due to one of the $A_{\text{g}}(M)$, and to what is referred to as $E_{\text{g}}(M)$ and $E_{\text{g}}(M)$ phonons with LA(M) phonons, or as recently proposed by Golasa et al [14, 15], with transverse acoustic (TA(M)) and/or out-of-plane TA (ZA(M)) phonons. We complement our analysis by exploring the multiphonon spectrum of monolayer 1H-MoS$_2$ (while leaving FL systems for later study) and anticipate that our full study will significantly advance fundamental understanding of the origin of multiphonon resonant inelastic light scattering processes in layered dichalcogenides and their application.

2. Experiment

Resonant Raman spectra for a bulk sample were measured in backscattering configuration using a Jobin-Yvon LabRam HR spectrometer with a He–Ne 632.8 nm laser (1.96 eV), which is slightly shifted in energy from the $\alpha$ exciton [18]. The scattered light was dispersed by a 1800 grooves/mm grating resulting in a $< 1$ cm$^{-1}$ spectral resolution. The low temperature spectra were measured at 95 K by means of a Linkam model THMS600 continuously-cooled liquid-nitrogen stage. UV-Raman was measured with He–Cd 325 nm laser (3.81 eV).

Off-resonant Raman spectra for bulk MoS$_2$ were also measured in the backscattering configuration using a Renishaw spectrometer with a 785 nm (1.58 eV) and a 514.5 nm (2.14 eV) lasers. Raman spectra measured at 1064 nm (1.16 eV) were acquired by using Bruker FT-Raman spectrometer. Raman spectra from a monolayer of MoS$_2$ were measured at 632.8 nm (1.96 eV). The power of the laser was kept sufficiently low to avoid heating effects.

Single and FL MoS$_2$ films were isolated from bulk MoS$_2$ crystals by mechanical exfoliation method and placed on a silicon substrate covered by a thick SiO$_2$ layer. After confirming that the distinctive Stokes Raman spectrum of the monolayer was consistent with previously published spectra [9], the monolayer thickness was verified by topographic-height scanning probe microscopy (Asylum Research MFP-3D).

3. Results and discussions

3.1. Symmetry mode analysis of multiphonon bulk 2H-MoS$_2$

In hexagonal MoS$_2$ there are six atoms in the unit cell and therefore 18 branches of the phonon dispersion relation, some of which are degenerate in high symmetry directions [19]. Table 1 presents a list of phonons in 2H-MoS$_2$ with their symmetry assignments, divided into the phonons symmetries at $\Gamma$ (BZ-center) and at M and K (zone-edge points in the $(\xi,0,0)$ and $(\xi,\xi,0)$ directions in $k$ space, respectively). For the $D_{\text{h}}$ space group the eigenstates at M and K points correspond to irreducible representations of the point groups $D_{2h}$ and $D_{3h}$, respectively. In table 1 we also show the frequencies of the various phonons. For the $\Gamma$ point we show experimentally measured frequencies at 300 K. For the M and K points the listed frequencies are the proposed values that are expected at low temperatures, in accordance with DFT calculations (and will be used to assign the resonant Raman spectrum at 95 K as described in section 3.2). We followed Sourisseau et al [17] in assigning the symmetry of the M point BZ phonons, while consulting the correlation tables between the point group of $D_{\text{h}}$ and its subgroups [20]. In labeling the symmetry of the representations we use the Mulliken notation [21]. Major aspects of constructing table 1 are discussed in the supporting information.

Each phonon branch is denoted with a letter (capital for $\Gamma$, greek alphabet for M and regular for K). The phonon notation $E_{\text{g}}(M_1)$, for example, denotes one of a doubly degenerate phonon at $\Gamma$ of $E_{\text{g}}$ symmetry, which splits and extends to M, where it has symmetry belonging to the $D_{2h}$ point group. We note that due to this splitting there are two different phonons at M ($M_1$ and $M_2$). Hence, the extensively used
notation [3–15, 16] of phonons at M that originate from doubly degenerate phonons at \( \Gamma \) (like \( E_{1g} (M) \) and \( E_{12g} (M) \)) is not suitable. In table 1 we also distinguish acoustic phonons as either LA, TA or ZA. We also denote the phonons at M originating as quasi-acoustic optical \( B_{2g}(\Gamma) \) and \( E_{2g}(\Gamma) \) phonons as ZA’ \( (B_{2g}(M)) \) and TA’ \( (E_{2g}(M)) + LA’ (E_{2g}(M)) \), respectively. The LA’ and TA’ phonons will be argued to be central in the multiphonon resonant process. At the K point all the phonons are assigned (see the supporting information) as singly degenerate, excluding the two doubly degenerate modes that originate from \( E_{1g}(M_1) + E_{2u}(M_2) \) and \( E_{2g}(M_1) + E_{1u}(M_2) \) (see supporting information).

Key in the analysis is the correlation of experiments with symmetry-based prediction of multiphonon transitions. Observation of high-order multiphonon processes demands accurate predictions. There are few published DFT calculations [22–24] that present the various phonon dispersions in \( 2H\)-MoS\(_2\). We extracted from those the calculated frequencies of the various M and K-point phonons. Correlating experiment with calculation, particularly for the M-point phonons, and noting that DFT estimates are for 0 K and will have at best a few % error in calculated mode energies, we introduce a tolerance of up to \( \pm 10 \text{ cm}^{-1} \) around the low temperatures measured value to facilitate the analysis. This is due to our ability

| Band | \( \Gamma/D_{3h} \) | \( \nu \) (cm\(^{-1}\))* | Band | \( M/D_{3h} \) | \( \nu \) (cm\(^{-1}\))* | Band | \( K/D_{3h} \) | \( \nu \) (cm\(^{-1}\))* |
|------|-----------------|-----------------|------|-----------------|-----------------|------|-----------------|-----------------|
| \( A (N) \) | \( B_{2g} \) | 475 | \( \alpha \) | \( B_{2g} \) | 393 | a | \( B_{2g} \) | 380 |
| \( B (IR) \) | \( A_{2g} \) | 470 | \( \beta \) | \( A_{2g} \) | 393 | b | \( A_{2g} \) | 380 |
| \( C (R) \) | \( A_{1g} \) | 409 | \( \chi \) | \( A_{1g} \) | 412 | c | \( A_{1g} \) | 402 |
| \( D (N) \) | \( B_{1u} \) | 403 | \( \delta \) | \( B_{1u} \) | 411 | d | \( B_{1u} \) | 402 |
| \( E (IR) \) | \( E_{1u} \) | 384 | \( \epsilon \) | \( E_{1u} \) | 370 | e | \( E_{1u} \) | 388 |
| \( F (R) \) | \( E_{1u} \) | 383 | \( \epsilon \) | \( E_{1u} \) | 362 | g | \( E_{1u} \) | 341 |
| \( G (N) \) | \( E_{2u} \) | 297 | \( \gamma \) | \( E_{2u} \) | 338 | h | \( E_{2u} \) | 338 |
| \( H (R) \) | \( E_{1g} \) | 286 | \( \eta \) | \( E_{1g} \) | 303 | i | \( E_{1g} \) | 342 |
| \( I (N) \) | \( B_{2g} \) | 58 | \( \iota \) | \( B_{2g} \) | 174 | k | \( B_{2g} \) | 184 |
| \( J (R) \) | \( E_{2g} \) | 35 | \( \varphi \) | \( E_{2g} \) | 160 | l | \( E_{2g} \) | 188 |
| \( K (AC) \) | \( E_{1u} \) | \( \kappa \) | \( E_{1u} \) | 235 | n | \( E_{1u} \) | 234 |
| \( L (AC) \) | \( A_{2g} \) | \( \lambda \) | \( A_{2g} \) | 182 | p | \( A_{2g} \) | 185 |

* Measured values at \(-300 \text{ K} \) [1–3].
# Proposed values at low temperatures (see text).

Table 1. A list of phonons of \( 2H\)-MoS\(_2\), their symmetry assignments and frequencies for M, K and \( \Gamma \) points in the Brillouin zone.
to ‘fine tune’ those frequencies by carefully looking at the resonant multiphonon bands, as shown below. Since some of the frequencies participate in several transitions involving high-order processes there is high sensitivity to our changes. Therefore the frequencies that we show in table 1 are proposed and should be considered as such. Indeed, the excellent fit between the predictions and the data for the M-point phonons indicates that those are very good predictions, particularly for the M point frequencies.

We next present a derivation of the symmetries of the Raman tensors of the second-order scattering from zone-edge phonons at M and K. We have listed in table 1 the symmetries of the individual phonons at Γ, M and K points. We next determine the irreducible representations of the binary combinations at each of

| Phonon combination | A'gxA'g | A'gxAu | A'gxB1g | A'gxB1u | A'gxB2g | A'gxB2u | A'gxB3g | A'gxB3u | A'gxA1g | A'gxA2g | A'gxE | A'gxE' |
|-------------------|------|------|-------|-------|-------|-------|-------|-------|-------|-------|------|------|
| A1gxA1g          | x    |      |       |       |       |       |       |       |       |       |      |      |
| A1gxA2u          |      | x    |       |       |       |       |       |       |       |       |      |      |
| A1gxB2g          |       |     | x     |       |       |       |       |       |       |       |      |      |
| A1gxB1u          |       |     |       | x     |       |       |       |       |       |       |      |      |
| A1gxE1g          |       |     |       |       | x     |       |       |       |       |       |      |      |
| A1gxE2g          |       |     |       |       |       | x     |       |       |       |       |      |      |
| A1gxE1u          |       |     |       |       |       |       | x     |       |       |       |      |      |
| A1gxE2u          |       |     |       |       |       |       |       | x     |       |       |      |      |
| A2gxA2u          |       |     |       |       |       |       |       |       | x     |       |      |      |
| A2gxB2g          |       |     |       |       |       |       |       |       |       | x     |      |      |
| A2gxB1u          |       |     |       |       |       |       |       |       |       |       | x     |      |
| A2gxE1g          |       |     |       |       |       |       |       |       |       |       |       | x     |
| A2gxE2g          |       |     |       |       |       |       |       |       |       |       |       |       | x   
| A2gxE1u          |       |     |       |       |       |       |       |       |       |       |       |       | x   
| A2gxE2u          |       |     |       |       |       |       |       |       |       |       |       |       | x   
| B2gxB2g          |       |     |       |       |       |       |       |       |       |       |       |       | x  
| B2gxB1u          |       |     |       |       |       |       |       |       |       |       |       |       | x  

Table 2. Group theoretical selection rules for two phonon Raman and IR activity from the Γ, M and K Brillouin zone points in bulk 2H-MoS2. The two active groups of symmetries are denoted with different colors. The scattering tensors of the Raman-active phonons are also shown.
these points. For the BZ-center phonons with $k = 0$ this is accomplished by simply multiplying together the characters of the individual group operations [25]. The determination of transitions for $k \neq 0$ phonons is less straightforward than that for $k = 0$, particularly for cases of non-symmorphic space groups, which are having glide planes and screw axis, e.g., space group #194, $D_{4d}^h$. Using the Bilbao crystallographic server [26] we obtained the Raman-active scattering tensors for second-order processes from phonons at M and K in the $D_{4d}^h$ space group and established the correlations between irreducible representations of the combinations of the group of a particular $k$ and the irreducible representations of the full space group. For a binary combination to be Raman-active at the M and K points it must correlate with at least one of the three Raman-active symmetries: $A_{1g}$, $E_{2g}$, and $E_{1g}$ of point group $D_{4d}^h$. For a binary combination to be IR-active at the M and K points it must correlate with at least one of the two IR-active symmetries: $A_{2u}$ and $E_{1u}$ of point group $D_{4d}^h$. Table 2 lists all the possible binary combinations for the M, K and $\Gamma$ points and their Raman and IR activity for 2H-MoS$_2$. Sets of scattering tensors of the Raman-active phonons are also shown. In order to construct them we reduced the products of binary combinations to their irreducible constituents and utilized the compatibility relations [26, 27] along $M \rightarrow \Sigma$, $K \rightarrow \Lambda$ and $M \rightarrow K$, as is briefly summarized in the supporting information.

All the modes in the M point (also for $\Gamma$) are either even or odd with respect to inversion (g or u, respectively). Hence, as is evidenced from table 2 the transitions of M point are divided into either Raman or IR activity. For the K point most of the bands show
activity on both. Furthermore, most of the M and K points second-order transitions that are active under parallel polarization backscattering configurations \((zx, xz)\) and \((zy, yz)\) in the Porto notation) are also active under perpendicular polarizations \((zx, yz)\) and \((zy, xz)\). We note that a significant fraction of the transitions \((\text{with } E_{1g} \text{ symmetry having } \alpha_{zx} \text{ and } \alpha_{yz} \text{ polarizability tensor components}) \) are expected to be active under off-resonant conditions only under tilted configuration, for which \(k \neq c\) axis (although we do not exclude their activity under resonant conditions at non-tilted configuration). Hence, besides those transitions that are forbidden as a result of being odd with respect to inversion, all the second-order transitions are Raman allowed, if we take into account the tilted scattering geometries as well. A detailed discussion and analysis of the polarized Raman spectra, in accordance with our extensive analysis, will be given elsewhere.

According to our analysis some of the assignments for second-order transitions at the M point \([3]\) that are currently cited in the literature are not symmetry allowed. This is because they are combinations of modes with different inversion symmetries \((g \text{ or } u)\); below we show the assignment and their symmetry products:

\[
A_{1g}(M) + L_A(M) \quad (A_g \times A_g), \quad E_{1g}(M) + LA(M) \quad (B_{3g} \times B_{3u}) \text{ and } \quad E_{1g}(M) + LA(M) \quad (B_{2g} \times B_{2u}) \text{, respectively).}
\]

In contrast, the symmetry products of the combinations that use instead the \(L_A\) phonon are symmetry allowed:

\[
A_{1g}(M) + L_A(M) \quad (A_g \times A_g), \quad E_{1g}(M) + LA(M) \quad (B_{3g} \times B_{3u}) \text{ and } \quad E_{1g}(M) + LA(M) \quad (B_{2g} \times B_{2u}) \]

### Table 3.

A proposed complete set of second-order phononic transitions from M and K Brillouin zone points in 2H-MoS\(_2\). Different groups of Raman scattering tensors are denoted, in accordance with tables 1 and 2, and are marked with different background colors. The upper number is for a combination and the lower one for a difference band (which are not shown below 70 cm\(^{-1}\)). In thick blue frames we denote M point Raman-allowed resonant second-order processes. The M point IR allowed combinations are denoted with white background.

| \(B_{3g}\) | \(B_{2g}\) | \(A_{1g}\) | \(B_{3u}\) | \(B_{1g}\) | \(E_{1g}\) | \(E_{2g}\) | \(A_{2g}\) | \(E_{3g}\) | \(A_{1u}\) | \(E_{1u}\) | \(E_{2u}\) | \(A_{2u}\) | \(A_{3u}\) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 393 | 374 | 393 | 412 | 411 | 370 | 362 | 362 | 370 | 160 | 160 | 233 | 96 | 160 |
| \(\bar{A}_{2g}\) | \(\bar{B}_{2g}\) | \(\bar{A}_{1g}\) | \(\bar{B}_{3u}\) | \(\bar{B}_{1g}\) | \(\bar{E}_{1g}\) | \(\bar{E}_{2g}\) | \(\bar{A}_{2g}\) | \(\bar{E}_{3g}\) | \(\bar{A}_{1u}\) | \(\bar{E}_{1u}\) | \(\bar{E}_{2u}\) | \(\bar{A}_{2u}\) | \(\bar{A}_{3u}\) |
| 786 | 219 | 786 | 808 | 804 | 763 | 751 | 751 | 763 | 558 | 558 | 233 | 131 | 558 |
| 348 | 567 | 386 | 386 | 585 | 544 | 536 | 536 | 544 | 334 | 334 | 307 | 407 | 334 |
| 786 | 805 | 805 | 805 | 763 | 751 | 751 | 763 | 553 | 553 | 522 | 625 | 553 | 522 |
| \(\bar{A}_{1u}\) | \(\bar{A}_{1g}\) | \(\bar{A}_{1g}\) | \(\bar{A}_{1u}\) | \(\bar{E}_{1u}\) | \(\bar{E}_{1g}\) | \(\bar{E}_{1g}\) | \(\bar{E}_{1u}\) | \(\bar{E}_{1u}\) | \(\bar{E}_{1u}\) | \(\bar{E}_{1g}\) | \(\bar{E}_{1g}\) | \(\bar{E}_{1g}\) | \(\bar{A}_{1g}\) |
| 824 | 823 | 824 | 823 | 782 | 774 | 774 | 782 | 572 | 572 | 522 | 645 | 572 | 522 |
| 824 | 823 | 824 | 823 | 782 | 774 | 774 | 782 | 572 | 572 | 522 | 645 | 572 | 522 |
| 824 | 823 | 824 | 823 | 782 | 774 | 774 | 782 | 572 | 572 | 522 | 645 | 572 | 522 |

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\[L A(M) + E_{1g}(M_{2}) + L A'(M) \quad (B_{2g} x A_{g} \quad \text{and} \quad B_{3g} x A_{g}'), \] respectively. However, we bear in mind that an alternative symmetry-allowed \(B_{2u} x B_{2u} \) combination with the \(LA(M)\) phonon \(E_{1u}(M_{1}) + L A(M)\) can be found at about the same frequency to that of the symmetry-forbidden combination of \(E_{1g}(M_{2}) + L A(M)\). The same can also apply to some of the other combinations/difference bands (with the \(B_{1u}(M)\) phonons) that may potentially contribute at about the same frequencies to those of the \(A_{1g}(M)\) phonons.

In the resonant spectrum, which will be shown below, and in our analysis henceforward, we consider the even-symmetry (with respect to inversion) second-order combinations/difference bands, which involve \(A_{1g}(M)\) and \(E_{2g}(M) \) (TA' (M)) and \(E_{2g}(M_{2}) \) (LA' (M)), which will be referred henceforward as the ‘resonant group’, are denoted in table 3 with a thick blue frame (see the supporting information for a comment on the nature of \(E_{1g}(M_{1})\)). All those combinations are also characterized by temperature-dependent intensity (not shown), clearly indicating their resonant nature (with the A exciton). The focus on those bands allows us to narrow down the possibilities in analyzing the intricate resonant Raman spectrum, which contains about 80 transitions in the spectral range of 80–1130 cm\(^{-1}\).

### Table 4.

Raman (colored) and IR (white) active combinations for second-order processes from phonons at \(\Gamma\) in 2H-MoS\(_{2}\) measured at 300 K. Different groups of Raman scattering tensors are denoted, in accordance with tables 1 and 2 and marked with different background colors. The upper number is for a combination and the lower one for a difference band (which are not shown below 70 cm\(^{-1}\)). The x sign denotes an inactive combination.

| \(A_{1g}\) 409 | \(A_{1g}\) 470 | \(B_{1g}^{1}\) 475 | \(B_{2g}^{1}\) 58 | \(B_{2g}^{2}\) 403 | \(E_{1g}^{1}\) 383 | \(E_{2g}^{2}\) 35 | \(E_{1g}^{2}\) 286 | \(E_{1g}^{3}\) 384 | \(E_{2g}^{2}\) 297 | \(\Gamma/D\alpha\) |
|---|---|---|---|---|---|---|---|---|---|---|
| 818 | 879 | X | X | X | 792 | 444 | 374 | 695 | 123 | 793 | X |
| 940 | X | X | X | X | X | 756 | 554 | 86 | 767 | 173 | A_{1g} 409 |
| 950 | 533 | 417 | 878 | 858 | 92 | 510 | 440 | 761 | 189 | X | 772 | B_{2g} 475 |
| 116 | 461 | 441 | 325 | 93 | 344 | 228 | X | 355 | B_{2g} 58 |
| 806 | 786 | 438 | X | 787 | 800 | 106 | B_{1u} 403 |
| 766 | 418 | 348 | 669 | 97 | 767 | 680 | E_{1g} 383 |
| 70 | 321 | 251 | 419 | 332 | E_{2g} 35 |
| 572 | 670 | 583 | E_{1g} 286 |
| 768 | 681 | 87 | E_{1g} 384 |
| 594 | E_{2g} 297 |

+ LA’(M) and \(E_{1g}(M_{2}) + L A' (M) \) \((B_{2g} x A_{g} \quad \text{and} \quad B_{3g} x A_{g}')\), respectively. However, we bear in mind that an alternative symmetry-allowed \((B_{2u} x B_{2u})\) combination with the \(LA(M)\) phonon \(E_{1u}(M_{1}) + L A(M)\) can be found at about the same frequency to that of the symmetry-forbidden combination of \(E_{2g}(M_{2}) + L A(M)\). The same can also apply to some of the other combinations/difference bands (with the \(B_{1u}(M)\) phonons) that may potentially contribute at about the same frequencies to those of the \(A_{1g}(M)\) phonons.

In the resonant spectrum, which will be shown below, and in our analysis henceforward, we consider the even-symmetry (with respect to inversion) second-order combinations/difference bands, which involve \(A_{1g}(M)\) and \(E_{2g}(M) \) (TA' (M)) and \(E_{2g}(M_{2}) \) (LA' (M)), which will be referred henceforward as the ‘resonant group’, are denoted in table 3 with a thick blue frame (see the supporting information for a comment on the nature of \(E_{1g}(M_{1})\)). All those combinations are also characterized by temperature-dependent intensity (not shown), clearly indicating their resonant nature (with the A exciton). The focus on those bands allows us to narrow down the possibilities in analyzing the intricate resonant Raman spectrum, which contains about 80 transitions in the spectral range of 80–1130 cm\(^{-1}\).

### 3.2. Resonant and off-resonant Raman scattering of bulk 2H-MoS\(_{2}\)

Shown in figure 1 is the Raman spectrum of 2H-MoS\(_{2}\) at 95 K, measured using excitation energy of 1.96 eV in the spectral range of 80–850 cm\(^{-1}\), and divided for clarity into four spectral sub-ranges (a–d). We also show positions of the second-order transitions’ bands (active under the backscattering configuration with \(k||c\) axis) of origin from M, K and \(\Gamma\) points, (tables 3 and 4). For \(\Gamma\), the estimated low-temperature frequencies
were obtained from measured values at room temperatures [1–3] after adding of ∼2.5 cm⁻¹ (taking an estimated typical shift of ∼0.012 cm⁻¹ K⁻¹ [5] for first-order phonons). For comparison the room temperature Raman spectrum using excitation energy of 1.58 eV is also shown (after being shifted in frequencies towards those of lower temperatures, for the sake of clarity). In order to highlight the second-order transitions at the M point that are due to the ‘resonant group’ the respective transitions are denoted by thicker blue marks. The rest of the M point group are denoted in red marks. It is clear from figure 1 that the majority of the prominent bands are attributed to the ‘resonant group’ at M. However, some of the prominent bands cannot be attributed to this group and the contribution of ‘off- resonant’ M and from K and Γ-point phonons must be taken into account. An example is the band at ∼756 cm⁻¹. Shown in figure 2 is the off-resonant Raman scattering spectrum around this band, measured at 300 K, and E₁g = 1.58 eV. In order to facilitate the discrimination of the large number of potential spectral contributions we compare the Stokes and anti-Stokes spectra (frequency is shown in absolute scale). The calculated frequencies of second-order transitions at M, K and Γ are also shown with the denoted respective colors. Black arrows are pointing to the central frequencies of the contributing bands. Significantly, some of the bands are masked in the Stokes spectrum and are ‘exposed’ in the corresponding anti-Stokes spectrum. The full spectral profile of the ∼756 cm⁻¹ band cannot be correlated exclusively with the M-point phonons. Clearly, some participation of K phonons and possibly Γ phonons is evident.

Finally, we emphasize that bands, which are very weak under resonant conditions, may become prominent in the spectrum, measured under off-resonant conditions. For example, the E₁g (M₁) + E₁g (M₂) combination may be responsible for the band which appears at ∼632 cm⁻¹ in the low side of the A₁g (M) + LA (M) [9]. This band becomes visible as we move away from resonance with the A exciton, either by altering the excitation energy (on both sides of the ∼1.9 eV resonance), or by increasing the temperature (as will be reported elsewhere).

Shown in figure 3 are sequences of all possible contributions (combination and difference bands) rendered in the form of ‘flowers’ for all the second (circles) and third (squares) order resonant transitions from the four ‘resonant group’ phonons. Processes

![Figure 1. The resonant Raman spectrum of 2H-MoS₂ at 95 K measured using excitation energy of 1.96 eV, divided for clarity into four spectral sub-ranges (a)–(d). Positions of the second-order transitions' bands of origin from M (‘Res’-blue, ‘Nonres.’-red), K (green) and Γ (magenta) Brillouin zone points, that are active under back scattering configuration, are also denoted. For comparison the room temperature Raman spectrum using excitation energy of 1.58 eV is also shown (pink). Note that for the band at ∼456 cm⁻¹, there is no possible assignment that may point to its origin.](image-url)
that lead to negative shifts (like LA′(M)–A1g(M)) are taken in their absolute values. At positions where neither is shown there is a process (e.g. A1g(M) + E2g(M2)−A1g(M)) which leads to first-order BZ-edge phonon scattering, and therefore not valid. Blue represents bands that are detected and red denotes bands not detected (possibly due to the low cross sections). Green represents a band that is possibly distinguishable or a band not found, but we believe may be observed under adequate conditions. For example the A1g(M)−E2g(M2) that are expected at 42 cm−1, below the filter cut-off. Furthermore, we expect this band to be strong, and examination of bulk spectra measured with Ei = 1.96 eV [28] reveals that it may be distinguishable. In fact, we anticipate that under resonance the following bands (and others that are not specified) may appear: 50 cm−1 (E2g(M2)−2TA′(M)), and 54 cm−1 (2LA′(M)−A1g(M)). Some of the other bands (marked in green) may be masked by other intense multiphonon bands.

The dominance of the ‘resonant group’ of phonons is expected particularly in the higher part of the spectrum where higher order transitions may be related exclusively with this group. Presented in figure 4(a) is a full set of up to 4th order contributions in the range of 830–1130 cm−1 for Ei = 1.96 eV at 95 K. The denoted bands are constructed from up to third order combinations of E1g(M2) (φ2) and A1g(M) (γ) phonons, subtracted or added to TA′(M) (φ2) or LA′(M) (φ2) phonons. In figure 4(b) the Raman spectra at 300 K for Ei = 1.96 eV and Ei = 1.58 eV are compared. The intensities of the high order bands decrease with an increase in temperature for Ei = 1.96 eV due to the departure from resonance [5], an observation that also affects lower-order multiphonon intensities [6]. In contrast, for Ei = 1.58 eV we find no spectral features beyond 825 cm−1, which is consistent with the attribution of that spectral range to resonant multiphonon processes. Other bands (like 2B1g(Γ) and 2A2h(Γ′)), which could potentially appear in this spectral range (see table 4), evidently have null (or very minor) contribution.

It is clear from figure 3 that, excluding A1g(M)−E2g(M2), all the possible second-order combinations of single degenerate phonons at M with an origin at Γ of A1g (I′), E2g (I′) and E2g (I) phonons: TA′(M) (φ1), LA′ (M) (φ2), E2g(M2) (φ2), A1g (γ) are observed in the resonant Raman spectra. In fact, many of the various third-order combinations are detected as well. Since the higher the scattering order the more quantitatively sensitive the spectral analysis, we further checked (beyond the presented spectrum in figure 4(a)) the consistency of the analysis by exploring the correlation between ‘expected’ and experimental band frequencies for a series of nA + mb (n = 0–3, A = γ, φ2, m = −1,0,1,2,3, B = φ1, φ2). In figure 5 we plot nA + mb versus mb for various n. We compare the calculated (‘expected’) and measured frequencies. The correlation between the two is excellent, as is evident from the fact that most of the of 30 bands that are ‘expected’ (up to the fourth order) within the range of 100–1150 cm−1 are detected with small discrepancy of ≤3 cm−1 between the calculated and measured values. Furthermore, higher order transitions are also detected in the room temperature spectrum, which was measured up to ~1400 cm−1 (see figure S1 in the supporting information).

In table 5 we list our proposed full assignment (most of which are resonant) of the up to fifth order multiphonon spectra (~80 transitions) measured up to ~1130 cm−1 at 95 K. It is important to note that additional bands, many of which are ‘masked’ by the intense resonant bands, are distinguishable under off-resonant conditions and warrant separate treatment guided by tables 1–4 that were provided above. Assigning the full spectral range is a complicated task, due to the significant overlap between many of the multiphonon bands that may originate from the I, M and K points and due to the need to take into account higher-order resonant transitions together with lower-order transitions that might be found in the same spectral position. The ability to be aided by temperature effects is in some cases limited under resonant conditions.

In table 5 we firstly assign the second order M-point bands of the above four phonons and of the ZA′ (i) phonon (see the supporting information for a
comment on the $E_{2g}(M_1) (\phi_1)$ phonon. The deviation between the measured frequencies and the ones shown in table 3 is $\leq 3 \text{ cm}^{-1}$. Then we assign the resonant third order process from the four phonons together with possible other second order M-point processes and also second order K and $\Gamma$—points phonons in accordance with tables 1, 3 and 4. Finally, we assign the spectral range above 825 cm$^{-1}$ (only observed under resonant conditions) with higher-order combinations constructed from M-point ‘resonant group’ phonons.

An important physical insight from this study, which presents a unified scenario consisting of symmetry analysis and quantitative band frequencies, is that the majority of resonant multiphonon combination processes is between M-point phonons that are from a branch that is optical at $\Gamma$. Furthermore, it seems that the cross sections for multiphonon bands that consist of $A_{1g} (M)$ contribution tend to be higher (as can be deduced by the larger portion of detected bands of higher than second order). Although their existence is clear, the dominance of the K contributed transitions is low with respect to those from the M point.

3.3. The nature of the Raman scattering ‘2LA band’

From the various bands the one denoted ‘2LA band’ is particularly interesting and following our analysis, this band now calls for reassignment. Previous resonance
Figure 4. (a) A full set of up to fourth order contributions in the range of 830–1130 cm$^{-1}$ for $E_i = 1.96$ eV at 95 K. The bands are constructed from up to third order combinations of $E_{1g}^2$ (M) ($\phi_2$) (blue) and $A_{1g}$ (M) ($\chi$) (red) phonons subtracted or added to $T_{A1}^\prime$ (M) ($\phi_1$) (dashed line) or $T_{A2}^\prime$ (M) ($\phi_2$) (solid line) phonons. Combinations of $E_{1g}^2 + A_{1g}$ (M) are shown in green. (b) A comparison of Raman spectra at 300 K for $E_i = 1.96$ eV and $E_i = 1.58$ eV.

Figure 5. A plot of $nA + mB$ versus $mB$ ($n = 0–3, A = \chi, \phi_2, m = -1,0,1,2,3, B = \phi_1, \phi_2$) for various $n$ of the calculated and the measured frequencies.
Raman studies on crystalline MoS\textsubscript{2} assigned this band to a second-order process involving the LA(M) phonon. The asymmetry of this peak was assigned to the inverse parabolic shape of the LA(M) dispersion curve near the M point in the BZ \cite{3}. Frey 	extit{et al} \cite{7} suggested that the asymmetric features of the

| Table 5. Proposed assignments of 2H-MoS\textsubscript{2} at low temperature (95 K), measured up to 1130 cm\textsuperscript{-1} using excitation energy of 1.96 eV. The notations are shown in table 1*.
|-----------------|-----------------|-----------------|-----------------|-----------------|
| \(\nu (\text{cm}^{-1})\) | Assignment | \(\nu (\text{cm}^{-1})\) | Assignment | \(\nu (\text{cm}^{-1})\) | Assignment |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 88 | \(\phi_1^2\phi_2\) | 405.5 | \(D\) | 739 | \(\phi_2^2\) |
| 92 | \(\phi_1^2\chi\) | 411 | \(C\) | 756 | \(\beta \varepsilon_2\) |
| 96 | \(\phi_2^2\phi_2\) | 428 | \# | 768 | \(\Gamma^2\) |
| 115 | \(I^2\) | 456 | \(S\) | 781.5 | \(\phi_2\chi\) |
| 118 | \(\phi_1\phi_2\chi\) | 466 | \(\phi_2^2\) | 788 | \(\phi_1^2\phi_2^2, \alpha^2, \beta^2\) |
| 125 | \(\gamma_2\varepsilon_2K_1\) | 470 | \(\kappa_1^2\) | 794.5 | \(\delta, \epsilon e\) |
| 137 | \(\overline{\theta}_2\phi_2\) | 478 | \(k^2\) | 802 | \(\chi\alpha\) |
| 142 | \(\phi_1^2\phi_2\chi\) | 479 | \(\phi_1^3\) | 808 | \(\phi_1\phi_2\chi\) |
| 151 | \(h^2\) | 485 | \(\overline{\theta}_1\phi_2\chi\) | 824 | \(\chi^2, \xi^2, \beta^2\) |
| 159 | \(\gamma_1^{\chi}\) | 501.5 | \(\phi_1^2\chi^2\) | 836 | \(\phi_2^2\phi_2\) |
| 168 | \(c\bar{m}\) | 514.5 | - | 850 | \(\phi_1^3\phi_2\) |
| 180.5 | \(\phi_2\chi\) | 530 | \(\phi_1\phi_2\) | 864 | \(\phi_2\chi^3\) |
| 192.5 | \(\phi_2^2\Gamma\) | 546 | \(\phi_2\Gamma\) | 877 | \(\phi_2^2\chi\) |
| 202 | \(\phi_1\phi_2\chi\) | 560.5 | \(\phi_2\phi_2^2\chi\) | 892 | \(\phi_2^3\chi\) |
| 210 | \(\phi_1\phi_2\) | 566 | \(\alpha\) | 901-947 | \(\phi_2^2, \phi_1\phi_2\) |
| 229 | \(\delta\chi, H\Gamma\) | 573 | \(\phi_1\chi\) | 958 | \(\overline{\theta}_2\phi_2\chi^2\) |
| 236.5 | \(\overline{\gamma}\chi\) | 576 | \(\beta \lambda, H^2\) | 973 | \(\phi_2^2\phi_2^2\) |
| 245 | \(\delta\kappa_2\) | 581 | \(\phi_1\phi_2^2\) | 984 | \(\phi_1\chi^2\) |
| 254 | \(\phi_1\chi\) | 591 | \(\phi_2\chi^2\) | 1000 | \(\phi_2\chi^3\) |
| 312 | \(\kappa_2^2\) | 603 | \(\phi_2\phi_2\) | 1013 | \(\phi_2\phi_2\chi\) |
| 319.5 | \(\phi_1^2\) | 620 | \(\phi_1\phi_2\chi\) | 1026 | \(\phi_2^3\phi_2^2\) |
| 329 | \(\phi_2^2\chi\) | 626 | \(\phi_1\phi_2^2, \phi_2\alpha\) | 1030 | \(\phi_1\phi_2\chi^2\) |
| 340 | \(\phi_1\phi_2\chi, \kappa_2\chi\) | 632 | \(c m, \eta_1\eta_2\) | 1043 | \(\phi_1\phi_2^2\phi_2^2\) |
| 347 | \(\overline{\iota}\) | 646 | \(\phi_2\chi\) | 1055 | \(\phi_2\chi^2\) |
| 356 | \(\phi_1^2\chi\) | 662 | \(\phi_1\chi^2\) | 1061 | \(\phi_1^2\phi_2^2\) |
| 365 | \(\lambda^2\) | 677 | \(\gamma_1^2\) | 1071 | \(\phi_2^3\phi_2\) |
| 383 | \(I^2, o^2\) | 684 | \(\overline{\tau}\) | 1111 | \(\phi_2^3\chi, \phi_2^3\) |
| 386.5 | \(F\) | 691 | \(\phi_1^2\phi_2\) | 1117 | - |
| 392.5 | \(\kappa_1\kappa_2\) | 700 | \(\phi_2^3\) | 1130 | \(\phi_1\phi_2\phi_2^2\) |
| 394.5 | \(\phi_1\phi_2\) | 709 | - |  |
| 398.5 | - | 725.5 | \(\phi_1^2\) |  |

*x and \(\overline{x}\) stand for addition and subtraction of a first-order \(x\) phonon and \(n \times \phi\) in \(x^n\) represents the order of the multiphonon transition of the \(x\) phonon.

# The ‘b band’ \cite{4, 5, 7}—see below in section 3.6.

$ See below the attribution of the ‘2LA band’ in section 3.3.
A ~460 cm\(^{-1}\) band is due to a combination of two peaks centered at room temperature at ~454 cm\(^{-1}\) (denoted here as \(\alpha_1\)) and ~465 cm\(^{-1}\) (\(\alpha_2\)). The first is assigned to the 2LA(M) and the second to a Raman-forbidden IR-allowed optical \(A_{2u}(\Gamma)\) mode, which involves asymmetric translation of both Mo and S atoms parallel to the \(c\) axis \([1]\). Unlike the \(\alpha_2\) band, which can be clearly assigned in figure 1, no feasible attribution to the \(\alpha_1\) band can be established (see the thick arrow in figure 1). Hence, there is a need to explore a different approach in order to trace its origin.

The phonon branches of bulk 2H-MoS\(_2\) in the vicinity of M and K points, calculated by Ataca \textit{et al} \([22]\), are shown in figure 6(a) with the respective extracted phonon density of states (PDOS). Figure 6(b) compares the spectra around ~460 cm\(^{-1}\) for various excitation energies \(E_i\) from 1.16 to 3.81 eV (dashed dotted line—a zoom of the smoothed lower band). The 2PDOS profile \([22]\) is shown in black line. (c) The \((\alpha_1/\alpha_2)\) intensity ratio is depicted for the set of measurements after adding the respective ratios for 1.16, 1.58, 1.91 \([13]\), 1.96, 2.09 eV (taken from \([6]\)) and 2.41 eV. The room temperature energies of the A and B excitons are also denoted.

In figure 6(c) the \((\alpha_2/\alpha_1)\) intensity ratio is depicted for the set of measurements after adding the respective ratios for 1.16, 1.58, 1.91 \([13]\), 1.96, 2.09 \([6]\) and 2.41 eV. The 2.09 eV measurement is particularly important because it is expected to match exactly the B exciton incoming resonance at 300 K. It is evident that in the vicinity of the A exciton around ~1.9 eV the ratio increases dramatically. Based on temperature dependent measurements (not shown) which indicate a significantly stronger resonant dependence of \(\alpha_2\) than for \(\alpha_1\), we conclude that there is a preferred resonance involving the A exciton for \(\alpha_2\). This, in turn, explains why we see such a strong signal from this band only for ~1.9 eV excitation. The reason for the much stronger excitonic resonance of A with respect to that of B for the \(\alpha_2\) band needs further theoretical clarification.

The resonant nature and characteristics of the high energy side of the of the ~460 cm\(^{-1}\) band for the 3.81 eV spectra is fundamentally different from that of the 1.96 eV spectra. For the latter \(E_i\), the \(\alpha_2\) band is constructed from second-order transitions at the M BZ point with no significant contribution of the \(A_{2u}(\Gamma)\) mode. For the former \(E_i\) the main contribution, according to a recently published elaborate study of Lee \textit{et al} \([30]\), comes from the \(A_{2u}(\Gamma)\) mode at
Evident that the spectra are comprised of at least five contributions, denoted in the figure as $A_1$, $A_2$, $A_3$, $A_4$, and $A_5$. The distinction between those contributions is not only enhanced as we shift $E_i$ with respect to the A exciton energy, but also as we depart from the resonance upon an increase in temperature. This can be seen in the inset of the lower part of figure 7 where we note the high similarity of the 2LA band taken at $E_i = 1.96$ eV and 573 K with the spectrum taken at room temperature and 1.58 eV. The resemblance of the spectral profile to that of the top spectrum taken at non-resonant conditions is evident.

For an appropriate assignment, it is important to realize that the M point is reached at $E_i = 3.81$ eV. Finally, the fact that the resonant behavior of the $A_2$ branch cannot be exclusively related with 2LA (M) may suggest that 2LA (M) band is also enhanced near the excitonic resonance. However, it is noteworthy that at lower temperatures (and $E_i = 1.96$ eV) the $L_3/(L_3 + L_4)$ intensity ratio is somewhat increased (will be shown elsewhere), which points to the former being slightly more resonant with respect to the latter.

3.4. Analysis of infrared-allowed second-order spectrum in bulk 2H-MoS$_2$

The group theoretical analysis done for the Raman scattering is complemented in tables 1–4 by the analysis of IR activity. Shown in figure 8 an IR
In what follows we show the spectral analysis for the monolayer while restricting ourselves to the $\Gamma$ and $M$ points. The eigenstates at those points correspond to irreducible representations of the point groups $D_{3h}$ and $C_{2v}$, respectively. Table 6 lists the various branches with their symmetries at the $\Gamma$ and $M$ points. In table 7 the Raman and IR activity of the various modes are specified and the polarizability tensors of the Raman-active phonons at the $\Gamma$ point are presented. For the $\Gamma$ point second-order transitions we find bands, which are either Raman- or IR-active, or both. For the $M$ point all the bands are both Raman- and IR-active. Unlike the phonon energies at $\Gamma$, which are known experimentally, at $M$ only calculated values are available, which seem to be within a few cm$^{-1}$ from the bulk values [22, 24]. We shall take the corresponding monolayer values to be similar to those of the bulk and employ the same procedure described above in tables 1–4 (see further details in the supporting information). Although the two are obviously not expected to be truly the same, it may be used as an estimation, in order to provide a guideline for the energies of the second-order transitions of the single layer $M$ and $\Gamma$ point phonons, which are shown in table 8.

Figure 9(a) presents the Raman spectrum of monolayer MoS$_2$ measured at $E_i = 1.96$ eV. Apart from the well-known first-order bands [8–10] we focus on the '2LA band' and compare it to the 2PDOS of the monolayer, calculated by Ataca et al [22] (after being shifted, for clarity, by a few cm$^{-1}$). Two distinct bands are apparent, which are also distinguishable in the 2PDOS. Similar to the bulk case, the correlation between the measured Raman and the 2PDOS is quite good. In line with the correlation with 2PDOS we tentatively assign the lower band to a van Hove singularity between $K$ and $M$, and the higher one to the 2LA (M)

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absorption spectrum previously measured by Wilson and Yoffe for a 180 $\mu$m layer of 2H-MoS$_2$ (figure 39 in [18]). The M point IR-allowed (Raman-forbidden) combinations (table 3) are also denoted. For the sake of clarity we do not show the $K$ and $\Gamma$ points IR-active combinations, but we bear in mind that those are also potentially contributors. In black stripes, the absorption bands from Agnihorti [31] are also indicated after subtracting from them 5 cm$^{-1}$ in order to take into account temperature effects (as they were measured in 77 K). Attached are proposed assignments to some of the bands. K point second-order potential contributors are not included.

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### 3.5. Symmetry mode analysis of second-order Raman scattering of monolayer 1H-MoS$_2$

Similar analysis to that of bulk 2H-MoS$_2$ can be made for monolayer 1H-MoS$_2$, for which the number of phonon dispersion relations is reduced from 18 to 9. The important differences lie in $i$. The fact that from each of the 2H Davydov doublets of the optical phonons ($B^{1}_{1g}$ and $A^{1}_{1g}$), ($A_{1g}$ and $B_{1u}$), ($E^{2}_{g}$ and $E_{1u}$) and ($E^{1}_{g}$ and $E_{2u}$) there is one branch left in the $\Gamma$ point of the 1H form with $A^\ast_{2g}$, $A', E$' and $E^\ast$ symmetries, respectively, $ii$. The branches at the M point that commence at $\Gamma$ and originate from the quasi-acoustic phonons of $B^{2}_{2g}$ and $B^{2}_{2g}$ ($L'A$, $T'A$ and $ZA'$ phonons) are absent in the monolayer.
and possibly also to a contribution of 2LA(K) (note the absence of LA′ phonons).

Recently Scheuschner et al [32] showed that the room temperature resonance Raman profile of the A′1 (Γ) phonon fits nicely to the A and B excitonic transitions for monolayer MoS2. In another recent study Pimenta et al [13] presented the Raman scattering excitation energy dependence for monolayer MoS2, from where it can be shown that the (α1/α2) intensity ratio follows the B excitonic transitions (the lowest excitation energy was 1.95 eV and therefore no conclusion can be drawn for the A exciton, which is centered at ∼1.84 eV). Hence, unlike the bulk, in the monolayer there is an enhancement of the α1 intensity with respect to that of α2. This result cannot be exclusively related with the absence of the LA′ phonons in the monolayer because in the bulk α2 does not show as well resonant enhancement in the vicinity of the B exciton. Further theoretical clarification is needed to explore the possibility of enhancement in the monolayer of the presumably 2PDOS mode.

In figures 9(c) and (d) we show the spectra of the monolayer in the energy range of 500–850 cm−1 and 110–280 cm−1, respectively, where second-order transitions are expected. The former is for overtones and combinations and the latter for the corresponding difference spectra. We denote in the figure the ‘expected’ positions of the various second-order bands that are due to A′1 (M), E′ (M1), E′ (M2) and LA (M) modes. By comparing the monolayer spectra with the bulk off-resonant 1.58 eV spectrum, we find that the two have substantial common characteristics and that the measured peaks correlate well with the expected energies listed in table 8. It is noteworthy that the 228 cm−1 band, which is absent in the 1.58 eV bulk spectrum, may be attributed to the A′1(M)–ZA (M) difference band, or, as recently proposed [33], to the LA(M) phonon.

3.6. A suggested reassignment of the ‘b band’ in MoS2

In a resonant Raman scattering study on a single crystal of 2H-MoS2 at T = 7 K and in the laser frequency range of 1.9 < Ei < 2.3 eV, Sekine et al [4] explored a highly dispersive band at 429 cm−1 denoted as the ‘b band’. The Stokes peak in that band has been interpreted in terms of a two-phonon process. The first phonon is the E11u phonon of finite wavevector and the second a B22g quasi-acoustic phonon (Δ2), which involves vibration of the S–Mo–S planes against each other. According to this interpretation the effect of varying the inorganic fullerenes (IF) diameter on the shift of the ‘b band’ was explained by Frey et al [7], and the effect of pressure and temperature on the ‘b band’ frequency and the ∼5 cm−1 shift between the Stokes and anti-Stokes frequencies of this band were analyzed in our previous publication [5].

There are two characteristics that should be fulfilled for the ‘b band’ interpretation [4] to apply: i. The exciting laser line is above the level of the A (or B) exciton. ii. The existence of the B22g mode, which appears in the bulk and not in the monolayer. From figure 9(a) it appears that the ‘b band’ is found in the Raman spectrum of the monolayer. Furthermore, like in the case of the bulk, the center frequency of the ‘b band’ in the anti-Stokes also shows a ∼5 cm−1 red-shift relative to

Table 6. A list of phonons of 1H-MoS2, their symmetry assignments and frequencies for Γ and M points in the Brillouin zone.

| Band | Γ/D_Mb | ν (cm−1) | Band | #ν (cm−1) | M/C2v |
|------|--------|----------|------|-----------|------|
| A (IR) | A′ 1 | ~470** | A′ 2 M | 393 | B1 |
| B (R) | A′ 1 | 403* | A′ 1 M | 412 | A1 |
| C (IR+R) | E′ | 384* | E M1 | 370 | A1 |
| D (R) | E′ | ~280** | E M2 | 362 | B2 |
| E (AC) | E′ | 0 | E M1 (LA) | 235 | A1 |
| F (AC) | A′ 2 | 0 | A′ 2 M (ZA) | 182 | B1 |

Measured (*) [8–10] or estimated (**) values at ~300 K.

* The frequencies for the M point are estimated.
Table 7. Group theoretical selection rules for two phonon Raman and IR activity from the $\Gamma$ and M Brillouin zone points in monolayer 1H-MoS$_2$. The three active groups of symmetries are denoted with different colors. The scattering tensors of the Raman active phonons are also shown.

| Phonon combination | $\Gamma$ | $\Gamma$ | $\Gamma$ | $\Gamma$ | $\Gamma$ | $\Gamma$ | $\Gamma$ | $\Gamma$ | $\Gamma$ | $\Gamma$ | $\Gamma$ | $\Gamma$ |
|---------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| $A_1^x A_1^y$      | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        |
| $A_1^x A_2^y$      | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        |
| $A_1^x A_2^y$      | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        |
| $A_1^x E_1^y$      | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        |
| $A_1^x E_2^y$      | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        |
| $A_2^x A_1^y$      | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        |
| $A_2^x A_2^y$      | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        |
| $A_2^x A_2^y$      | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        |
| $A_2^x E_1^y$      | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        |
| $A_2^x E_2^y$      | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        |
| $A_2^x E_2^y$      | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        | x        |

As a consequence of these new findings (the actual ‘appearance’ of this band in monolayer and its characteristics), a suggested alternative assignment of the

that found in the Stokes. Moreover, it seems that the intensity of the ‘b band’ in the monolayer shows some excitonic resonant dependence (see figure 4 in [13]).
‘b band’ is desirable. With the aid of the newly constructed table 3 we seek for a possible attribution of the transitions that are found at low temperatures in bulk MoS$_2$ at $\sim 423$ and $\sim 428$ cm$^{-1}$ in anti-Stokes and Stokes spectra, respectively [4, 5]. For the M point the only possible attribution is LA$^\prime$(M) + ZA (M) at $\sim 417$ cm$^{-1}$, which is too low with respect to the experimental values. For the K point we find LA$^\prime$′(K) + TA (K) /TA$^\prime$′(K) at $\sim 427$ cm$^{-1}$, and LA (K) + TA (K)/TA$^\prime$′(K) at $\sim 424$ cm$^{-1}$, which are within the expected frequencies and are also shifted by $\sim 3$ cm$^{-1}$. We also note that LA$^\prime$′(K) + ZA (K)/ZA$^\prime$′(K) and LA (K) + ZA (K)/ZA$^\prime$′(K) (which contain only the E$_{1g}$($\Gamma$) representation under our scheme) are expected at $\sim 422$ cm$^{-1}$, and $\sim 419$ cm$^{-1}$, respectively. Although the frequencies at the K point had not been satisfactorily verified to match the experimental data (since most of the attributed transitions are from the M point), we can still suggest that the ‘b band’ is more likely related with second-order phonon at the K point.

We may therefore suggest that the ‘b band’ is constructed from two bands, for which their peaks were not well separable in previous studies [4, 5, 7]: the higher band/s (LA$^\prime$′(K) + TA (K)/TA$^\prime$′(K) or LA (K) + TA (K)/TA$^\prime$′(K)) is resonant with the A exciton and is more pronounced in the Stokes outgoing resonance [5], and the lower band is constructed from the contribution/s of combination band/s: (LA$^\prime$′(K) + ZA (K)/ZA$^\prime$′(K) or LA (K) + ZA (K)/ZA $^\prime$′(K)). For the monolayer case the phonons LA(K) + TA(K) and LA (K) + ZA(K) may be considered. Hence, the resonant activation of the upper band (that is minor in the anti-Stokes side) may be related with what we considered as a large blue shift of this mode in the Stokes with respect to the 'less resonant' anti-Stokes side.

Additional support of the proposed reassignment can be found in figure 9(b), which compares the Stokes and anti-Stokes spectra of 2H-MoS$_2$, measured at $E_i$ = 1.58 eV and at room temperature. There are clearly two weak bands at $\sim 422$ and $\sim 417$ cm$^{-1}$ in the similar spectral positions of the room temperature 'b band' in the Stokes and anti-Stokes spectra, measured at $E_i$ = 1.96 eV. The appearance of these bands, which are presumably correlated with the 'b band', is not consistent with the full requirements needed for the currently available interpretation [4, 5, 7] to be valid. This is because $E_i$ is significantly lower than the A exciton energy. Furthermore, it seems that unlike for the resonant $E_i$=1.96 eV case, the $\sim 5$ cm$^{-1}$ shift between the two major bands is not observed in the spectra of $E_i$ = 1.58 eV and the two modes appear in about the same spectral positions in both Stokes and anti-Stokes spectra. This new proposed alternative interpretation of the 'b band' remains to be substantiated further. It is particularly important (and challenging) to separate the seemingly hardly-resolved contributions of the sub-bands that construct the 'b band' in spectra measured under resonance.

| $E_i$ | $A_2^\prime$ | $A_1$, $E^\prime$ | $E^\prime$ | $E^\prime$ | $E^\prime$ | $A_2^\prime$ | $E_2$, $E^\prime$ | $E_2$, $E^\prime$ |
|------|-------------|-----------------|----------|----------|----------|-------------|-----------------|-----------------|
| 393  | 805         | 763             | 755      | 699      | 723      | 628         | 737             | 760             |
| 412  | 782         | 744             | 718      | 106      | 742      | 647         | 728             | 753             |
| 370  | 700         | 676             | 700      | 135      | 605      | 530         | 687             | 710             |
| 362  | 636         | 541             | 597      | 127      | 522      | 446         | 510             | 542             |
| 366  | 512         | 540             | 490      | 170      | 512      | 466         | 488             | 512             |
| 330  | 490         | 512             | 466      | 146      | 488      | 432         | 364             | 342             |
| 235  | 403         | 395             | 364      | 190      | 364      | 320         | 342             | 320             |
| 160  | 384         | 451             | 320      | 257      | 342      | 320         | 342             | 320             |
| 182  | 280         | 190             | 560      | 104      | 560      | 190         | 560             | 190             |

Table 8. A complete set of second-order phononic transitions from M and $\Gamma$ Brillouin zone points in monolayer 1H-MoS$_2$. The upper number is for a combination and the lower one for a difference band (which are not shown below 70 cm$^{-1}$). The frequencies of the M point are the estimated ones (based on the assumed resemblance of the 1H and 2H frequencies). Different groups of Raman scattering tensors are denoted, in accordance with tables 6 and 7 and are marked with different background colors.
4. Conclusions

To summarize, we present a comprehensive analysis of multiphonon Raman spectrum in MoS$_2$. The low temperature resonant spectra were measured with excitation energy of 1.96 eV, which is slightly shifted in energy from the $A$ exciton. The analysis consists of symmetry assignments, from which we obtain a broad set of allowed second-order transitions at high-symmetry points in the BZ.

(1) An important physical insight from this study, is that in the bulk the majority of multiphonon resonant bands are proposed to originate from combination processes between to four BZ edge phonons at M that are from branches that are optical at $\Gamma$ (with $A_{1g}$ ($\Gamma$), $E_{2g}$ ($\Gamma$) and $E_{2g}$ ($\Gamma$)). Consistent with the fact that at the M Brillouin edge only combinations with the same inversion symmetry (g or u) are Raman-allowed, the contribution of combinations with the LA (M) mode can not be considered with the four phonons that were assigned to construct the 'resonant group': $A_{1g}$ (M), $E_{2g}$ (M$_2$), $E_{2g}$ (M) (TA' (M)) and $E_{2g}$ (M$_2$) (LA' (M)). Among the four phonons, all (but one which is not experimentally detectable in our system) of the second order overtones, combination and difference-bands and many of the third order bands, are found in the low temperature resonant Raman spectra.

(2) As a complemented study we extended the analysis infrared allowed second-order transitions. We also present a multiphonon analysis of the M and $\Gamma$ points for monolayer 1H-MoS$_2$. Correlation between the analysis and room temperature Raman spectrum measured at 1.96 eV is satisfactory.

(3) We demonstrate that the '2LA band' at $\sim$460 cm$^{-1}$ measured at 1.16–2.41 eV is constructed from at least five Lorentzian contributions. Supported by the striking similarity between this band, measured under off- resonant conditions, and the 2PDOS [22], we propose the reassignment of the lower part of the band ($\alpha_1$), that was previously attributed to 2LA(M), to a van Hove singularity between K and L.
M and the higher part (α₂) to mostly the LA and LA’ phonons at the M point. The $A_{2u}(\Gamma)$ mode is activated under excitations with considerably higher energy of 3.81 eV (and evidently also with 2.81 eV [30]). Similar approach applies for monolayer 1H-MoS₂.

We anticipate that this analysis will promote the understanding of the currently unresolved mechanism of the multiphonon scattering in MoS₂ and its intricate excitation energy dependence. It may as well inform the interpretation of similar processes from a range of other layered dichalcogenides.

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