

Influence of sulfur vacancies on the high frequency phonon modes of ALD-grown monolayer MoS₂Jonathan Rommelfangen  and Alex Redinger Department of Physics and Materials Science, *University of Luxembourg*, Luxembourg, LuxembourgMarco Antonio Gonzalez-Angulo Center for Industrial Electronics, *University of Southern Denmark*, Alsion 2, Sønderborg, DenmarkDevendra Pareek and Levent Gütay Institute of Physics, *Carl von Ossietzky University of Oldenburg*, Oldenburg, Germany

(Received 17 June 2025; revised 22 August 2025; accepted 4 November 2025; published 19 December 2025)

Precise control of defects in two-dimensional materials is crucial for their application in functional devices. Raman spectroscopy is a key technique for identifying the number of layers and strain in MoS₂. Changes in the peak area ratio of the Raman active modes A_{1g} and E_{2g}^1 measured on monolayer (ML) MoS₂ have, so far, only been correlated to changes in the excitation wavelength of the laser, i.e., resonant effects. However, the role of sulfur vacancies (V_S) on this peak area ratio is not well studied. In this study, we show on ALD-grown MoS₂ that changes in the peak area ratio of the A_{1g} and E_{2g}^1 Raman modes depend sensibly on the number of V_S in the film. Raman measurements carried out with three different excitation wavelengths are combined with detailed x-ray photoelectron spectroscopy measurements to quantify the number of V_S in the film and to study their impact on vibrational properties. V_S -poor MoS₂ displays a stronger A_{1g} mode compared to the E_{2g}^1 mode, whereas the ratio is reversed in V_S -rich films. We propose that this effect originates from modifications in the electronic band structure of ML MoS₂. Based on this experimental work, we propose that the peak area ratio of the A_{1g} and E_{2g}^1 modes could be used as a fingerprint for the qualitative evaluation of the S deficiency in MoS₂ MLs, which could be an easy-to-apply method for the quality assessment in industrial applications.

DOI: [10.1103/kzhl-5sy6](https://doi.org/10.1103/kzhl-5sy6)

Two-dimensional (2D) materials, specifically transition metal dichalcogenides (TMDs), possess unique properties compared to their bulk counterparts, making them attractive for applications like transistors [1–3], solar absorbers [4,5], hydrogen production [6,7], and optoelectronics [8,9]. Controlling defects and impurities is critical for achieving desired properties, as shown for hydrogen evolution [6,7], single-photon emission [10], and metal-semiconductor contacts [11]. While thickness can now be controlled on wafer scales [12–17], the (un)intentional inclusion of vacancies and their control remains a big challenge. Their identification often requires high-resolution methods like transmission electron microscopy (TEM) [18,19] or scanning tunneling microscopy (STM) [20], which are incompatible with industrial manufacturing processes. Here, we demonstrate that Raman spectroscopy can detect sulfur vacancies (V_S) in monolayer (ML) MoS₂, a 2D material of high technological relevance. The Raman-active phonon modes A_{1g} and E_{2g}^1 are well studied, and their peak separation is commonly used to determine layer number [21,22]. However, there is a complex interplay between the intensity ratio, peak position, and peak distance of

these modes and they depend strongly on the synthesis method [16,21,23–31]. Figure 1(a) reveals a considerable variation of the peak area ratio in the literature [16,21,23–29]. The dotted line marks the transition where the peak area of the E_{2g}^1 mode switches from being larger than the peak area of the A_{1g} mode to being smaller. The most common observation, namely, A_{1g} showing a larger peak area, is, therefore, found on the right side of the line. In Fig. 1(b) the peak area ratio is also plotted against the excitation wavelength used to measure the Raman signals. Figure 1 reveals considerable variation in the reported ratios, highlighting the need for deeper understanding. Since Raman scattering is assisted by electrons, it is sensitive to excitation wavelength and resonance with the electronic band structure [Fig. 1(b)]. For the excitation wavelengths from 532 nm to 488 nm the reported ratios do not show a clear trend.

At 354 nm and 266 nm, Hsiang *et al.* [26] reported notable changes attributed to variations in resonant conditions and electronic band-structure interactions as the optical absorption near the Γ -point and intervalley resonant electronic scattering by M -point phonons become significant under these conditions, altering the intensity of the Raman modes [26]. These effects were not seen by Hong *et al.* [25] and Placidi *et al.* [29] at 325 nm, who observed only second-order resonance for the 325-nm excitation. This discrepancy might stem from different V_S concentrations: Hong and Placidi used mechanically exfoliated samples, while Hsiang used chemical vapor depo-

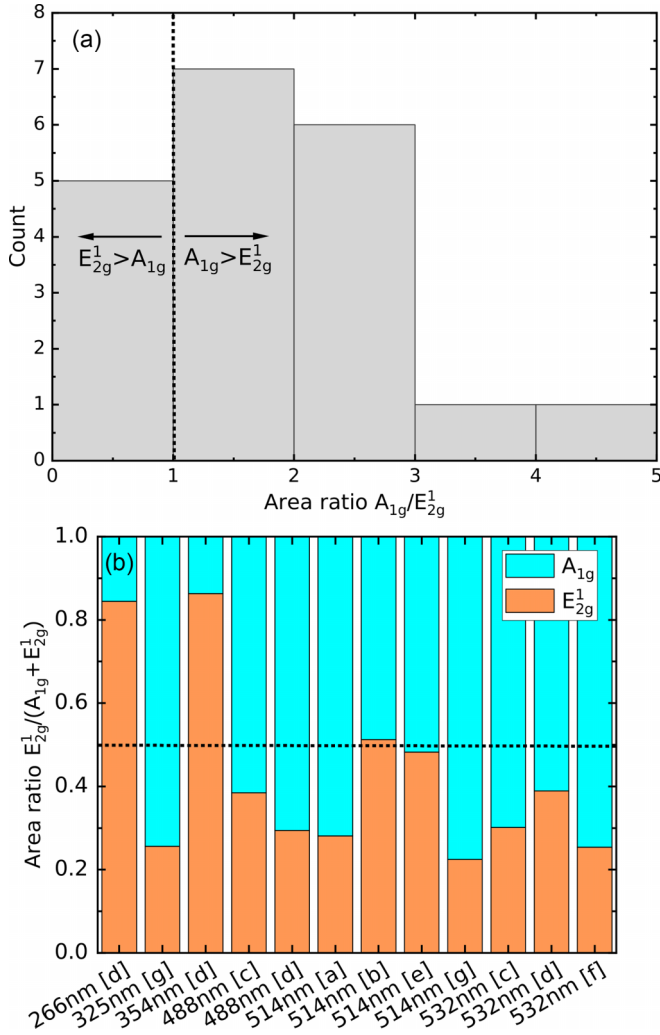


FIG. 1. (a) Literature-reported peak area ratios ($\frac{A_{1g}}{E_{2g}^1}$). The dotted line marks the ratio with equal peak areas [16,21,23–29]. (b) Peak area ratios ($\frac{E_{2g}^1}{A_{1g} + E_{2g}^1}$) as a function of excitation wavelength. All data are from mechanically exfoliated ML MoS₂ on SiO₂, except for (d) which is CVD grown. Reference (a) is from [23], (b) [24], (c) [25], (d) [26], (e) [21], (f) [28], and (g) [29].

sition (CVD)-grown MoS₂, which typically contains more V_S [18]. None of the authors linked it to V_S and it is exactly this question that will be answered in this work. A complete review of the effects of the synthesis method, the substrate, and the excitation wavelength on the peak distance, the peak area ratio, and the position of the E_{2g}^1 and A_{1g} modes appears in the Supplemental Materials [32], Figs. 1 to 3.

The defects in ML MoS₂ can come in many forms [33–35], with point defects significantly impacting the material properties of MoS₂ [33–35], such as in-gap states [20,36,37]. V_S are the most common, having the lowest formation energy [18,33,38,39]. Density functional theory (DFT) calculations predict formation energies of 1.3 to 1.5 eV in *S*-poor environments [38], while experiments report 0.71 eV [10]. Thus, V_S are intrinsic to CVD and atomic layer deposition (ALD)-grown MoS₂ [18,19,33]. ALD-grown ML MoS₂ typically exhibits intrinsic V_S concentrations from $1.2 \times 10^{13} \text{ cm}^{-2}$

to $4 \times 10^{13} \text{ cm}^{-2}$ [18,19], which can be varied via vacuum annealing [40] or ion irradiation [41]. The MoS₂ atomic structure does not show significant distortion up to $1 \times 10^{15} \text{ cm}^{-2}$ [41]. To remove V_S, a high-temperature annealing in a sulfur-containing atmosphere was reported [15,42,43].

We show that V_S concentrations can be tuned through ultra-high vacuum (UHV) or sulfur-rich annealing and quantified via x-ray photoelectron spectroscopy (XPS). Raman spectra taken from exactly the same samples reveal changes in A_{1g} and E_{2g}^1 modes, linking them directly to the V_S concentration of the ML MoS₂.

The ML MoS₂ films were synthesized via ALD using H₂S and MoCl₅ as precursors followed by a postgrowth sulfurization to reduce the intrinsic V_S density. Full details are given by Gonzalez *et al.* [44]. To ensure surface cleanliness, samples were UHV-annealed at 380° C prior to all processing steps, effectively removing surface contaminants as confirmed by XPS (see Fig. 15 in the Supplemental Material [32]). V_S were introduced by thermal annealing in UHV at 500° C, a method previously reported [10], as V_S preferentially form under *S*-poor conditions due to their low formation energy [10,38]. Healing was achieved by evaporating sulfur from FeS₂ at 400° C under 10^{-6} mbar, while substrates were held at 360° C, for 120 minutes. The details are elaborated on by Hall *et al.* [45]. Measurements were performed on the exact same sample after each treatment step (V_S-healed, UHV-annealed, V_S-rehealed), using conductive atomic force microscopy (c-AFM), XPS, and Raman spectroscopy. To prevent oxidation [36,46,47], all transfers occurred under UHV or N₂ atmosphere. c-AFM was conducted in contact mode with a Scienta Omicron VT-AFM in UHV. XPS was measured in a Prevac EA15 hemispherical analyzer and an Al K α source (1486.6 eV). Raman spectra were measured in N₂ with 442 nm (2.82 eV), 532 nm (2.33 eV), and 633 nm (1.96 eV) lasers at low power densities (2.47 mW, 2.53 mW, and 1.75 mW, respectively, and a laser spot diameter of $\approx 1 \mu\text{m}$) at which no alterations of the sample and measurements were observed, even after a longer and repeated irradiation of the sample.

Figure 2(a) depicts XPS data from the V_S-poor sample (after synthesis and annealing in a sulfur containing atmosphere) composed of multiple oxidation states of the Mo 3*d* doublet. The S in oxidation state 2– and Mo in oxidation state 4+ correspond to MoS₂. The defective MoS₂ peak is represented by the Mo 3*d* (2+) oxidation state corresponding to Mo bonded to a single S atom. The full width at half maximum (FWHM), Mo/S ratio and peak positions were calibrated using a UHV-cleaved single-crystal of MoS₂ as elaborated on in Sec. 4 of the Supplemental Material [32]. An artifact arising from the layered structure of MoS₂ leading to attenuation effects for the photoelectrons from the bottom sulfur atom layer could be ruled out and is discussed in detail in Sec. 14 in the Supplemental Material [32]. The peak ratio and distance of Mo 3*d* doublets are determined by the spin-orbit coupling and they are constant for a certain orbital and element [48–53]. So each oxidation state of Mo 3*d* was fitted with the same FWHM, peak position, and ratio. The values can be retrieved from databases [52,53]. The stoichiometry of the V_S-poor film, as determined by fitting the XPS intensities, was Mo_{0.93}S_{1.93} indicating 3.5 at.% V_S, which corresponds to a concentration

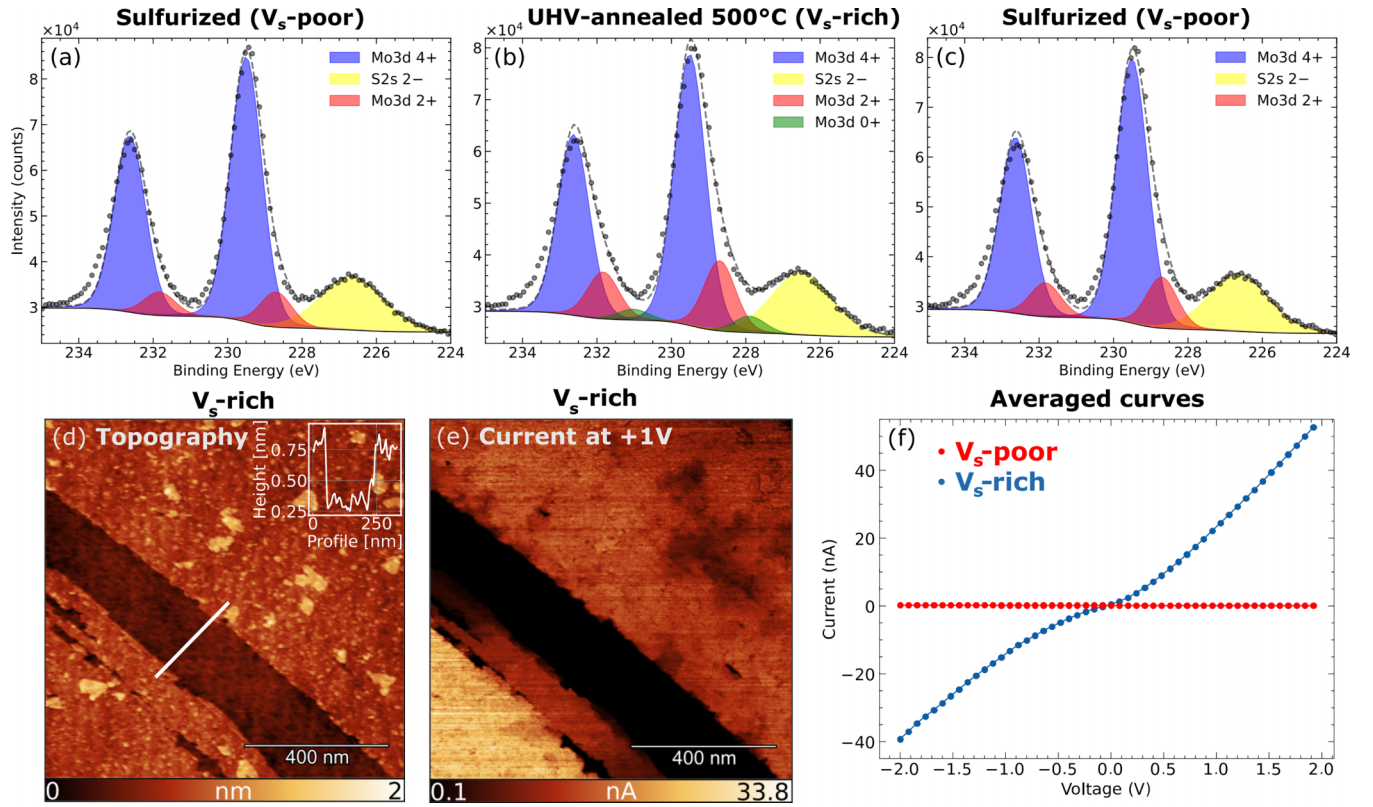


FIG. 2. Mo 3d XPS spectra of ML MoS₂ following sulfurization (V_S -poor) and UHV-annealing (V_S -rich). (a) First sulfurization: Mo₁S_{1.93} (V_S -poor). (b) After UHV-annealing: Mo₁S_{1.8} (V_S -rich). (c) Recovered to Mo₁S_{1.9} (V_S -poor) after second sulfurization. (d) Topography and (e) current map at +1V of V_S -rich MoS₂. The current and topography maps are displayed in a linear scale colorbar. (f) Averaged I-V curves for V_S -rich (blue) and V_S -poor (red) MoS₂.

of $8 \times 10^{13} \text{cm}^{-2}$. This value was close to the values in the literature of the intrinsic amount of V_S synthesized via CVD [18,40].

After the 500°C UHV-annealing (V_S -rich) the amount of V_S increased to 10 at.% (Mo₁S_{1.8}), with more Mo 3d (2+) and some metallic Mo [see Fig. 2(b)], which corresponds to a defect concentration of $2.3 \times 10^{14} \text{cm}^{-2}$. The XPS results, therefore, suggest that the high-temperature UHV-annealing produced additional V_S . To show that the V_S concentration could be changed back to the original state, a second sulfurization was done, and the XPS results are shown in Fig. 2(c). The stoichiometry recovered to Mo₁S_{1.9} proving the healing of the V_S . Importantly the metallic Mo was also removed, which showed that the sulfur atmosphere did not only fill V_S , but could also convert the Mo back into MoS₂. To support that the changes observed via XPS were indeed vacancy-induced, c-AFM was used to measure local changes in conductivity. Since V_S act as donors [35,54,55] an increase in V_S concentration should change the conductivity of the films. Measurements were taken on both V_S -rich and V_S -poor samples. Since the current in c-AFM depends sensitively on the tip geometry and the contact area a reference measurement was needed. A scratch introduced with a diamond tip exposed the insulating c-plane sapphire substrate [Fig. 2(d)]. A scratch approximately 300 nm in width was observed. From the height profile [inset of Fig. 2(d)] a step height of $0.5(\pm 0.1)$ nm was measured which confirmed ML thickness.

The current map of the V_S -rich MoS₂ (UHV-annealed) in Fig. 2(e) shows no current on the scratched region (uncovered sapphire), but approximately 20 to 30 nA on the surrounding MoS₂, indicating conductivity due to defects, which is confirmed by the Kelvin probe force microscopy (KPFM) measurements in Sec. 11 in the Supplemental Material [32], which suggest that the V_S -rich MoS₂ is *n*-type. The higher current below the scratch (bottom left corner) is an artifact due to local tip-sample contact variations, which is discussed in detail in Sec. 11 in the Supplemental Material [32]. The same was done for the sulfurized sample (see Fig. 7 in Supplemental Material [32]). Figure 2(f) compares the average I-V curves of the V_S -rich (blue) and V_S -poor (red) MoS₂. The V_S -rich film showed a clear current-voltage curve, which was completely absent for the V_S -poor film. The c-AFM results align with the XPS data, confirming tunable V_S concentrations. The next section explores their impact on the Raman peak area ratio of the A_{1g} and E_{2g}^1 modes.

At each stage of the sample treatment (see Fig. 3), Raman spectroscopy was performed on three regions several mm apart using 442 nm, 532 nm, and 633 nm lasers. $10 \times 10 \mu\text{m}^2$ mappings with a laser spot diameter of 1 μm confirmed spatial uniformity. In the Supplemental Material [32], Figs. 10 and 11 is a detailed analysis of the mappings. The peaks were fitted with symmetric pseudo-Voigt functions and identified using literature data [29,56].

Figure 3(a) shows the V_S -poor spectrum measured with the 442-nm laser, where the A_{1g} peak area exceeds the area of the

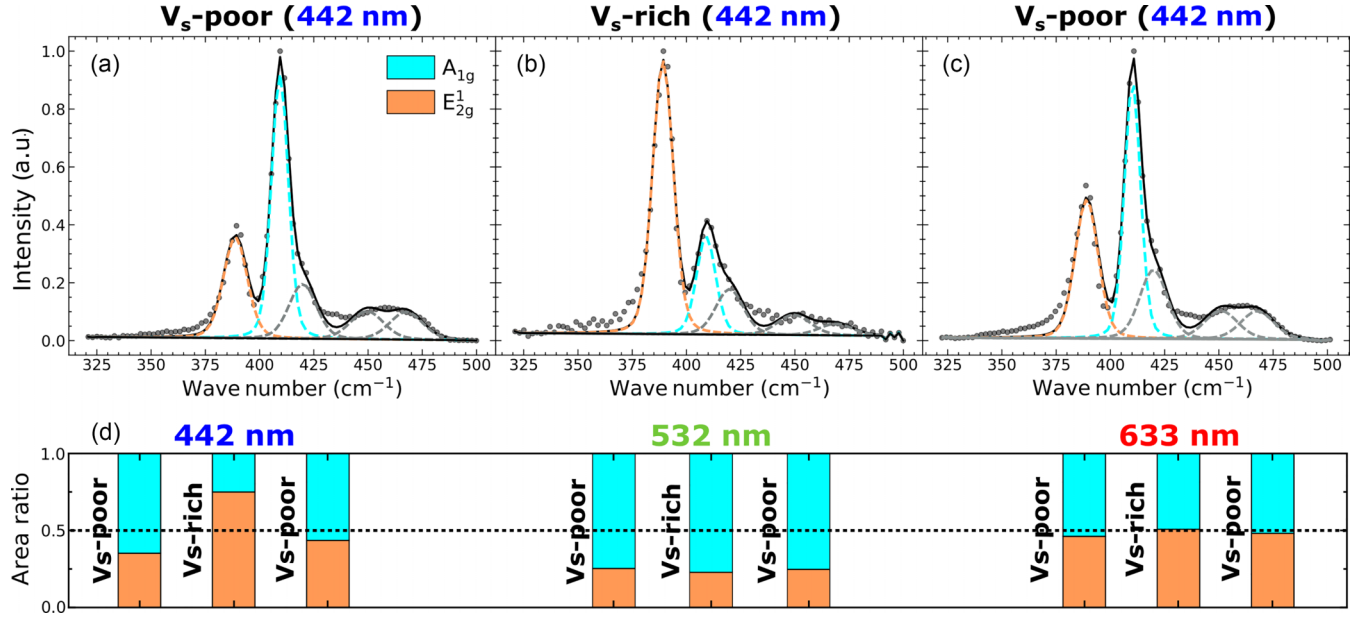


FIG. 3. Raman spectra of the ML MoS₂ after (a) first sulfurization (V_S-poor), (b) 500 °C UHV-annealing (V_S-rich) and after (c) second sulfurization (V_S-poor). (d) Peak area ratio ($\frac{E_{2g}^1}{A_{1g}+E_{2g}^1}$) for V_S-rich and V_S-poor MoS₂ for the three different excitation wavelengths.

E_{2g}^1 mode, as mostly reported in the literature [see Figs. 1(a) and 1(b)]. After 500 °C UHV-annealing (V_S-rich), this ratio inverted [Fig. 3(b)]. A subsequent sulfurization (V_S-poor) restored the original ratio, where the area of the A_{1g} mode was larger again [see Fig. 3(c)]. As all measurements were performed on exactly the same sample, process-dependent variations could be excluded. The effect of area ratio switching was also observed on a sister sample undergoing the same treatment (see Supplemental Material [32], Fig. 16). In addition to the E_{2g}^1 and the A_{1g} mode, the spectra contained a sapphire related contribution (424 cm⁻¹), the 2LA mode (450 cm⁻¹), and the A_{2u} mode (468 cm⁻¹) from MoS₂. The latter two varied with V_S concentration, though only A_{1g} and E_{2g}^1 were analyzed due to intensity limitations.

No inversion of the peak area ratio ($\frac{E_{2g}^1}{A_{1g}+E_{2g}^1}$) occurred with the 532-nm and 633-nm excitation wavelength [see Fig. 3(d)] where variations were within the fitting error. This is supported by mapping the data in the Supplemental Material [32], Figs. 10 and 11. The fitted spectra of the 532-nm and 633-nm excitation can be found in the Supplemental Material [32], Fig. 8. The change in peak positions, FWHM, and the peak distance were not significant (see the Supplemental Material [32], Figs. 9 and 12). V_S-related Jahn-Teller distortions were not observed in our Raman measurements. Further discussion is provided in Sec. 10 of the Supplemental Material [32].

We conclude that the peak area ratio ($\frac{E_{2g}^1}{A_{1g}+E_{2g}^1}$) correlates with the V_S concentration. Its excitation wavelength dependence suggests that the origin of the effect is due to variations in the electronic band structure. DFT studies confirm that V_S significantly affect the vibrational properties and electronic structure of MoS₂ [57,58]. Removing sulfur atoms weakens the restoring force constants for in-plane vibrations, leading to a softening (red-shift) of the E_{2g}^1 mode, as theoretically

predicted [57]. However, we do not observe this red-shift, aligning with several studies at similar V_S concentrations [40,59]. Yang *et al.* [41] did not observe significant changes up to 10 at.%. V_S introduce localized gap states, acting as electron traps or bound excitons, thereby modifying electron-phonon interactions [58,60]. In our specific case, at approximately 10 at.% V_S concentration, under 442-nm excitation, the usually dominant A_{1g} mode intensity is reduced, while the E_{2g}^1 mode intensity is comparatively enhanced, creating a ratio inversion. Crucially, this inversion does not occur at 532-nm or 633-nm excitations, consistent with previous reports that highlight that defect-induced Raman intensity changes are sensitive to resonant conditions [26,61]. Thus, the defect levels in our MoS₂ do not significantly affect Raman scattering at A-exciton (≈ 1.9 eV) or B-exciton (≈ 2.0 eV) energies but rather at higher energies. Specifically, the 442-nm (2.81 eV) excitation wavelength is in resonance with the C-exciton region (≈ 2.8 eV) of ML MoS₂ [61], where the intensity of the main first-order Raman peaks (E_{2g}^1 and A_{1g}) is enhanced in pristine MoS₂ [56]. However, in the presence of V_S, new resonant Raman scattering pathways could become possible. We propose that under 442-nm excitation, vacancy-induced electronic states resonate with this wavelength, preferentially amplifying scattering from the in-plane E_{2g}^1 mode. This resonance with the defect-induced band structure could increase the E_{2g}^1 mode Raman cross-section relative to the A_{1g} mode. There is one study that could show experimentally that the change in peak area ratio changes on pristine MoS₂ with the excitation wavelength [26]. In this study the reversal in peak area ratio ($\frac{E_{2g}^1}{A_{1g}+E_{2g}^1}$) only occurred for the ultraviolet laser (354 nm or 3.5 eV). A theoretical study by Miranda *et al.* showed a similar effect on MoTe₂ [62]. The reason why we observed this switch in the peak area ratio ($\frac{E_{2g}^1}{A_{1g}+E_{2g}^1}$) already

with the 442-nm (2.81 eV) excitation wavelength strongly suggests that the formation of V_S changed the C -exciton region and the associated continuum. When their transition energy becomes, after V_S formation, resonant with the 442 nm (2.81 eV), but not with the 532-nm (2.33 eV) and the 633-nm (1.96 eV) excitation wavelength we have a good explanation for the excitation wavelength dependent peak area ratio change upon V_S formation.

In conclusion, Raman spectroscopy of the high frequency phonon modes A_{1g} and E_{2g}^1 , that changed in the peak area ratio ($\frac{E_{2g}^1}{A_{1g}+E_{2g}^1}$), was reproducibly correlated with the formation of V_S , which has not yet been reported, to the best of our knowledge. This approach, that involved to keep the MoS_2 at anytime in a protective environment allowed us to exclude oxidation and contamination from this effect. We could show that the usage of the 442-nm excitation wavelength could be an easy method to confirm whether the ML MoS_2 is V_S -rich or V_S -poor, at least for a V_S density threshold of $2.3 \times 10^{14} \text{ cm}^{-2}$ or higher, by using the area ratio as a fingerprint. This proof-of-concept opens up a pathway to easier tailoring of MoS_2

properties for applications where V_S concentration is critical, such as the hydrogen evolution reaction (HER), and could represent a valuable advancement for nanotechnology and materials engineering of MoS_2 and related TMDs. It would be highly desirable in future work to extend this approach to other synthesis routes, such as CVD or mechanical exfoliation, to further establish the generality of this Raman fingerprint method.

J.R. and A.R. gratefully acknowledge funding by the Luxembourg National Research Fund (FNR), Grants No. 13584473 and No. 11244141. Useful discussions with Evandro Lanzoni and Jeremy Hieulle are acknowledged. The technical support from Bernd Uder, Ulrich Siegel, and Robert Himelrick is acknowledged.

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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