First-principles study on structural, thermal, mechanical and dynamic stability of T’-MoS₂

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Abstract
Using first-principles density functional theory calculations, we investigate the structure, stability, optical modes and electronic band gap of a distorted tetragonal MoS₂ monolayer (T’-MoS₂). Our simulated scanning tunnel microscopy (STM) images of T’-MoS₂ are dramatically similar to those STM images which were identified as K₂(H₂O)₆MoS₂ from a previous experimental study. This similarity suggests that T’-MoS₂ might have already been experimentally observed, but due to being unexpected was misidentified. Furthermore, we verify the stability of T’-MoS₂ from the thermal, mechanical and dynamic aspects, by ab initio molecular dynamics simulation, elastic constants evaluation and phonon band structure calculation based on density functional perturbation theory, respectively. In addition, we calculate the eigenfrequencies and eigenvectors of the optical modes of T’-MoS₂ at Γ point and distinguish their Raman and infrared activity by pointing out their irreducible representations using group theory. At the same time, we compare the Raman modes of T’-MoS₂ with those of H-MoS₂ and T-MoS₂. Our results provide useful guidance for further experimental identification and characterization of T’-MoS₂.

Keywords: simulated STM images, first-principles, physical stability, Raman and infrared modes, T’-MoS₂

((Some figures may appear in colour only in the online journal)
[7, 10]. T'-MoS2 is thought to be a charge density wave (CDW) state as a result of the Piers phase transition from T phase [23]. The structural stability of T'-MoS2 was first inferred from formation energy by Kan et al [7]. They found that the formation energy of T'-MoS2 is higher than that of H-MoS2 but lower than T-MoS2. Namely, that T'-MoS2 is a meta-stable phase. Qian et al calculated the phonon band structure of T'-MoS2 and found no imaginary frequency, which confirmed the vibrational stability of T'-MoS2 [24]. However, as to the stability of T'-MoS2 in other physical respects, such as the thermal and mechanical stability, has not yet, to the best of our knowledge, been studied theoretically. Although previous experimental studies have reported the observation of T'-MoS2 phase identified by experimental STM images [25, 26], those STM images, however, have not been sufficiently explicit to demonstrate the existence of T'-MoS2. In addition, a discrepancy is also presented with respect to the band gap of T'-MoS2. For instance, T'-MoS2 was first predicted to be a semiconductor with a narrow band gap [7, 24]. In contrast, the electronic band structure given by Gao et al implied that T'-MoS2 was a semimetal [27].

Therefore, a theoretical study on the physical stability and electronic properties of T'-MoS2 is urgently necessary. In the present work, we perform DFT calculations within local density approximation (LDA) to investigate the simulated STM images, the stability and the electronic band gap of T'-MoS2. The simulated STM images provide a significant reference for identifying the lattice structure from experimental STM images. The ab initio molecular dynamics (AIMD) simulations confirm the thermodynamic stability of T'-MoS2 at room temperature; the calculating results of elastic constants meet the Born–Huang criteria, which implies the mechanical stability of T'-MoS2; the absence of the imaginary frequency in the phonon dispersion relation indicates the vibrational stability of T'-MoS2. Besides, we also classify the optical modes by group theory and compute their corresponding eigenfrequency and eigenvector, which play an important role in the identification and characterization of T'-MoS2 phase from optical experiment. Moreover, we make a contrast calculation of the electronic band structure to determine the effect of the spin–orbit coupling, which clarifies the origin of band gap of T'-MoS2.

The remainder of this paper is organized as follows. In section 2, methodology and computational details are described. Section 3 presents first the simulation of STM imaging of MoS2 in three different phases, then the stability of T'-MoS2 is explored from different aspects. The symmetry classification of the vibrational modes along with their eigenfrequency and eigenvector are then calculated. Furthermore, the electronic band structure and band gap of T'-MoS2 are investigated by considering the spin–orbit coupling. Finally, conclusions are drawn in section 4.

2. Methodology

Both total energy and electronic band structure calculations were performed by using the Vienna ab initio simulation package (VASP) [28, 29]. The electron–ion interaction was described by using the frozen-core projector augmented wave (PAW) method; [30, 31] the exchange and correlation were treated with generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) form [32]. Besides standard DFT with GGA, the hybrid Heyd–Scuseria–Ernzerhof (HSE)06 method [33, 34], was also employed to give a more accurate description of the band gap of T'-MoS2. In the HSE06 method, a fraction of the exact screened Hartree–Fock (HF) exchange is incorporated into the PBE exchange using a mixing parameter \( \alpha = 0.25 \). We used a cutoff energy of 300eV for the plane wave basis set, which yields total energies convergence better than 1 meV/atom. The Van der Waals interactions are treated with the empirical correction scheme of Grimme’s DFT-D2 method, which has been successful in describing the geometries of various layered materials [35, 36].

In the slab model of single-layer MoS2, the periodic slabs were separated by a vacuum layer of 15 Å in the c direction to avoid mirror interactions. A \( 10 \times 5 \times 1 \) k-mesh including \( \Gamma \)-point, generated according to the Monkhorst–Pack scheme [37], was applied to the Brillouin-zone (BZ) integrations. Through geometry optimization, both the shapes and internal structural parameters of pristine unit-cells were fully relaxed until the residual force on each atom was less than 0.01 eV/Å.

To examine the stability of the modeled structure of T'-MoS2 from the lattice dynamics point of view, the force-constant approach involving a finite displacement was adopted as employed by the PHONOPY [38] code. The force constant matrix was calculated with a \( 7 \times 4 \times 1 \) supercell containing 168 atoms, based on the density functional perturbation theory (DFPT) method [39] implemented into VASP. Furthermore, the phonopy codes also enable us to obtain the eigenfrequency and eigenvector of lattice vibrational modes at the center of BZ.
The simulated STM images were generated by using the P4VASP package, which can facilitate the simulation of STM image with a continuously varying scanning distance. The theory for simulating STM imaging by \textit{ab initio} density functional calculations is well established \cite{40}. Giving a small bias voltage $V_b$ between the sample and the STM tip produces a tunneling current, whose density $j(r)$ can be obtained from a simple extension \cite{41} of the expression derived by Tersoff and Hamann \cite{42, 43}:

\[ j(r, V_b) \propto \rho_{\text{STM}}(r, V_b), \]  

(1)

where \[
\rho_{\text{STM}}(r, V_b) = \int_{E_F}^{E_b} \rho(r, E) dE \]  

(2)

and

\[ \rho(r, E) = \sum_{n,k} |\psi_{nk}(r)|^2 \delta(E_{n,k} - E). \]  

(3)

Here, $\rho(r, E)$ is the local density of states at the center of the tip at $r$ and $\psi_{nk}(r)$ are the electron eigenstates of the unperurbed surface at energy $E_{n,k}$. These eigenstates are commonly represented by Kohn–Sham eigenstates obtained using DFT. The assumption behind this is that the relevant tip states are described by $s$ waves with a constant density of states \cite{41–43}. Furthermore, the tunneling matrix element is considered to be independent of both the lateral tip position for a constant tip-to-surface distance and the bias voltage $V_b$ in the narrow (but nonzero) energy region $[E_F - eV_b, E_F]$. Equation (3) describes tunneling from the occupied states of the sample to the tip. The simulated STM image is not sensitive to the bias voltage as long as the valance band enters in the integral range, but is sensitive to the scanning distance from the tip to the sample surface.

Simulating STM imaging has been used for studying the modification of the electronic structure of the 2H phase MoS$_2$ (0001) surface produced by several point defects \cite{44}. Recently, it was also used for exploring a few-layer phosphorus capped by a graphene and hexagonal boron nitride monolayer \cite{45}. In present work, we apply this method to study the structure of single-layered MoS$_2$. Different bias voltages $V_b$ are used for the distinct phases of monolayer MoS$_2$ according to their electronic properties. For H-MoS$_2$, its band gap is 1.7 eV, and its Fermi level is under the conductor band at about 0.1 eV, so that the value of bias voltage $V_b$ is set to 1.8 V, and thus the energy range $[E_F - eV_b, E_F]$ enters the valance band at about 0.2 eV. As with metallic T'-MoS$_2$, we have compared the simulated images using two different bias voltages (0.3 and 1.8 V), but find no significant distinction, hence we always use the smallest one in the following calculations. For T'-MoS$_2$, its band gap is merely 0.1 eV, so a bias voltage $V_b = 0.5$ V is enough.

### 3. Results and discussion

#### 3.1. Simulated STM images and identification of monolayer MoS$_2$

We begin our discussion by comparing the simulated STM images of the three possible structures, namely, H, T, and T' phases of monolayer MoS$_2$ \cite{46}. The lattice structures of the three phases are displayed in figure 1. The most energetically favorable H-MoS$_2$ (as shown in figure 1(a)) has a sandwich-like structure of three planes of 2D hexagonally packed atoms, S-Mo-S, where Mo atoms are trigonal-prismatically coordinated by six S atoms, forming ABA stacking with P6m2 space-group symmetry. In contrast, the Mo atoms in the T-MoS$_2$ (as shown in figure 1(b)) structure are octahedrally coordinated with the nearby six S atoms, resulting in ABC stacking with P3m1 space group symmetry. H- and T-MoS$_2$ phase have very different electronic properties: the former is a large gap semiconductor, but the latter is a metal. It has been predicated that the T-MoS$_2$ is typically unstable in the free-standing condition \cite{7, 19}. T-MoS$_2$ should undergo the Piers distortion in one direction to form a $2 \times 1$ super-lattice structure, consisting of

![Figure 2. Simulated STM images of monolayer MoS$_2$. (a)–(c) are simulated images of H, T, and T' phases, respectively, where the purple and yellow spheres represent Mo and S atoms.](image)

![Figure 3. Simulated STM images of T'-MoS$_2$ with different scanning distances. (a) the scanning distance $d = 6.59$ Å and (b) the scanning distance $d = 5.74$ Å.](image)
one-dimensional zigzag Mo-Mo chains along the other direction, i.e. the T'-MoS₂ phase, as shown in figure 1(c). It implies theoretically that T'-MoS₂ should be more stable than T-MoS₂ in free-standing conditions. In the experiments, however, Eda et al have observed both T- and T'-MoS₂ by scanning transmission electron microscopy (STEM) imaging [25], but the image of T'-MoS₂ is not as clear as that of T-MoS₂. Although WS₂ and MoTe₂ monolayer have been found experimentally [47, 48], T'-MoS₂ has not been identified unanimously, to the best of our knowledge, in experiments yet. Therefore, we perform an ab initio density functional calculations to simulate STM images of MoS₂ monolayer in the three phases. Figure 2 shows the calculated STM images of H-, T-, as well as T'-MoS₂, respectively. Our simulated STM images agree well with those images obtained in previous experiments [25]. This agreement indicates the reliability of the simulated STM imaging method.

The scanning distance \( d \) represents the distance from the scanning plane to referring plane, and the referring plane is put on the upper surface of crystal cell in slab model of MoS₂ monolayer. The scanning distance is denoted in terms of the tip position in P4VASP. To determine the influence of the scanning distance on STM imaging, we perform the simulating STM imaging calculations varying continuously the scanning distance. It is found that the simulated STM images vary remarkably with the scanning distance. This variation even may lead to the misidentification of the experimental STM images [49]. On one hand, it means that we may obtain quite different STM images which actually belong to the identical structure in experiment, as seen in figure 3, in which we have shown the top and side view at two different scanning distances, while the tip position for the middle plane of the MoS₂ monolayer is \( d = 3.39 \) Å. Then the distances from scanning plane to the middle plane are 3.20 Å and 2.35 Å, respectively. If merely judging from the top view of the simulation images without referring the other information, you might think that the lower sublet of figure 3(a) represents T'-MoS₂ phase, but that of figure 3(b) belongs to the image of T-MoS₂. On the other hand, it also means that the different phases of MoS₂ may have similar STM images. Comparing the simulated images of T-MoS₂ and T'-MoS₂ with appropriate scanning distances presented in figure 4, you may find it is hard to distinguish these two phases. Thus, we should not make identification using only single experimental STM image without any other information.

Knowing this, how can we identify the lattice structure of STM image in the experiment? The method is to scan the STM images while varying the tip-to-surface distance. By comparing and contrasting those images, you can make the correct identification, as the different structures have distinct changing patterns. This suggestion is deduced from our STM imaging simulation of T-MoS₂ and T'-MoS₂ with continuously varying scanning distance. The structural symmetry of a simulated image of T-MoS₂ remains invariant as the scanning distance varies consecutively, in contrast, that of T'-MoS₂ varies significantly, just as demonstrated in figure 3. It is worth mentioning that the STM images obtained experimentally are usually scanning within one or two given tip-to-surface distances. Then a question arises: whether it is possible that the structure of MoS₂ observed in previous experiments could be T' phase rather than T phase?

It is natural to examine the relevant experiments in literature, and we find that the answer is affirmative. In an experimental STM imaging study of T-MoS₂ [11], there are several STM images in figures 2 and 3 in [11], which were identified as \( K_x(H_2O)_yMoS₂(x < 0.3) \). We make the corresponding simulation of T'-MoS₂, which are shown in figure 5. Comparing our simulated STM images of T'-MoS₂ phase with these images, we find that the simulated images are in surprising accord with the experimental STM images. This dramatic accordance indicates strongly that these experimental images should be corresponding to T'-MoS₂ phase rather than \( K_x(H_2O)_yMoS₂ \). That is to say, the T'-MoS₂ has been synthesized accidentally, but unfortunately misidentified. If this was true, it actually means an experimentally feasible method for synthesizing T'-MoS₂, which is important for the fabrication of a novel topological field effect transistor [24].

The instability of free standing T-MoS₂ at 0K is revealed by imaginary frequency presented in its phonon dispersion relations from the recent first-principles calculations [19, 20]. At the same time, several theoretical and experimental researches show that the function of alkali metal is to offer an extra electron to make the T-MoS₂ phase more stable in energy [17]. While in [11], the presence of water stabilizes the T' phase from the original high symmetric structure [15, 21, 50, 51]. Therefore, the method designed to obtain T-MoS₂ is actually a feasible method to produce T' -MoS₂ in experiment. For reliably identifying T'-MoS₂ in experiment, it is necessary to exploit the stability of T'-MoS₂.

3.2. Thermal stability of T'-MoS₂

The thermal stability of T'-MoS₂ is explored by performing AIMD simulations using a canonical ensemble. To reduce the constraint of periodic boundary condition, the T'-MoS₂
is simulated by $3 \times 2$ super-cells. The snapshots of T’-MoS$_2$ atomic configurations for the final stages of AIMD simulations at 300 K and 800 K are shown in figures 6(a) and (b), respectively. One can find that no significant reconstructions are observed at 300 K and 800 K. Here the only exception in the latter case is that the S and Mo atoms are found to be slightly moved due to thermal fluctuation. This means that T’-MoS$_2$ can withstand the higher temperature at least up to 800 K, implying the high-energy barriers between T’ phase and H phase, which is in consistent with the first-principles calculations performed by Qian et al [24].

### 3.3. Mechanical stability and anisotropy of T’-MoS$_2$

Since the super-cell is fixed during the MD simulations, we have to evaluate the effect of elastic distortion on structural stability. In order to guarantee the positive-definiteness of strain energy following lattice distortion, the components of linear elastic modulus tensor of a stable crystal must obey the Born–Huang criteria [52]. We calculate the change of energy due to the in-plane strain to examine the mechanical stability of T’-MoS$_2$. For a 2D crystal, the elastic strain energy per unit area can be written as [53]

$$U(\varepsilon) = \frac{1}{2} C_{11} \varepsilon_{xx}^2 + \frac{1}{2} C_{22} \varepsilon_{yy}^2 + C_{12} \varepsilon_{xx} \varepsilon_{yy} + 2C_{66} \varepsilon_{xy}^2,$$  

(4)

where $C_{ij}$ are the components of the elastic modulus tensor using the standard Voigt notation (i.e. 1-xx, 2-yy, and 6-xy) [54], corresponding to second partial derivative of elastic energy with respect to strain. The elastic constants can be derived by fitting the energy curves associated with uniaxial and equibiaxial strains. Under uniaxial strain applied along x direction, $\varepsilon_{xx} = \varepsilon_0$, this leads to $U(\varepsilon) = \frac{1}{2} C_{11} \varepsilon_{xx}^2$. Parabolic fitting of the uniaxial strain curve yields $C_{11} = 109.0 \text{GPa} \cdot \text{nm}$. Similarly, under uniaxial strain applied along y direction, $C_{12} = 124.0 \text{GPa} \cdot \text{nm}$. Under equibiaxial strain, $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_0$, one has $U(\varepsilon) = (\varepsilon_0^2) \left( \frac{1}{2} C_{11} + \frac{1}{2} C_{12} \right)$. By fitting the equibiaxial strain curve, we obtain $C_{11} + C_{12} = 130.9 \text{GPa} \cdot \text{nm}$, which means that $C_{12} = 14.4 \text{GPa} \cdot \text{nm}$. For a mechanically stable 2D crystal, the elastic constants should satisfy two criteria: $C_{11}C_{22} - C_{12} > 0$ and $C_{66} > 0$ [52]. For T’-MoS$_2$, one can easily verify that the calculated components of the elastic modulus tensor satisfy $C_{11}C_{22} - C_{12} > 0$; besides, the calculated $C_{66} = 38.8 \text{GPa} \cdot \text{nm}$ is positive. Both the two criteria of mechanical stability are met, thus the mechanical stability of T’-MoS$_2$ is confirmed.

Due to its lower point group symmetry, T’-MoS$_2$ has an anisotropic elastic property, which is significantly different from H- and T-MoS$_2$. Both H- and T-MoS$_2$ are of isotropic elastic properties described by two elastic constants: Young’s modulus $Y$ and Poisson’s ratio $\nu$. The Young’s modulus and Poisson’s ratio of T’-MoS$_2$, however, do not remain constant, but vary with orientation. The formula for Young’s modulus $Y(\theta)$ and Poisson’s ratio $\nu(\theta)$ are [52, 55]

$$Y(\theta) = \frac{C_{11}C_{22} - C_{12}^2}{C_{11}s^4 + C_{22}c^4 + \left( \frac{d_{15}^2 - d_{12}^2}{c_6} \right) - 2C_{12}s^2 c_6},$$  

(5)

$$\nu(\theta) = \frac{C_{12} + \left( \frac{d_{15}^2 - d_{12}^2}{c_6} \right) - 2C_{12} - C_{11} - C_{22}}{C_{11}s^4 + C_{22}c^4 + \left( \frac{d_{15}^2 - d_{12}^2}{c_6} \right) - 2C_{12}s^2 c_6},$$  

(6)

Figure 6. Snapshots of atomic configurations of T’-MoS$_2$ at the end of AIMD simulations from front, top, and side views, respectively. The simulated super-cells are marked by black squares, and their corresponding temperature and time are denoted above each panel.
where \( s = \sin(\theta) \) and \( c = \cos(\theta) \), \( \theta \) is the the angle with respect to the \( x \)-axis. The above two formulas are universal for all orthogonal 2D crystal.

Their extremum directions can be determined by analyzing the zeros of the first derivative of \( Y(\theta) \) and \( \nu(\theta) \). Generally, there are three extremum directions for both \( Y(\theta) \) and \( \nu(\theta) \), in which there are two same extremum conditions: \( \sin(\theta) = 0 \) and \( \cos(\theta) = 0 \), which means that the coordinate axes directions \( x \) and \( y \) (rather, the symmetrical principal axes directions) are extremum directions. we find that for \( Y(\theta) \), both the two axes may maximum (or minimum) directions, meanwhile, for \( \nu(\theta) \), they must be both minimum (or maximum) directions. Certainly, the two maximum (or minimum) directions mean that there must be one minimum (or maximum) direction between the two axes. Depending on the relative value of elastic constants, the third extremum between the two axes for \( Y(\theta) \) may not exist, then one axis direction is the maximum and the other the minimum direction. For Poisson’s ratio, the third extremum always exists, except for isotropic case. The above conclusions about extremum direction are also universal for orthogonal 2D crystal structures.

Here, we plot the curves of \( Y(\theta) \) and \( \nu(\theta) \) in polar coordinates for \( T'\text{-MoS}_2 \) in figure 7, which intuitively show the elastic anisotropy of \( T'\text{-MoS}_2 \). First, it can be seen that the extremum directions are consistent with our analyses above. Second, it can be found that the variation range of Young’s modulus is from about 96.9–124.0 GPa · nm, the value of Poisson’s ratio is limited between 0.117 and 0.25. Third, it can be found that the principal minimum direction of \( Y(\theta) \) is along \( \theta = 39.5^\circ \) and the maximum direction of \( \nu(\theta) \) for \( T'\text{-MoS}_2 \) are almost along a diagonal direction.

3.4. Lattice dynamic stability and vibrational modes of \( T'\text{-MoS}_2 \)

3.4.1. Lattice dynamic stability. To further verify the lattice dynamic stability of the \( T'\text{-MoS}_2 \), we calculate phonon dispersion relation of \( T'\text{-MoS}_2 \) and demonstrate it in figure 8. We can note that the phonon dispersion of \( T'\text{-MoS}_2 \) has three acoustic and fifteen optical branches. The three acoustic branches are the in-plane longitudinal acoustic (LA), the transverse acoustic (TA), and the out-of-plane acoustic (ZA) branches. The LA and TA branches have linear dispersion and a higher frequency than the ZA mode around \( \Gamma \) point in the Brillouin zone. In contrast to \( H\text{-MoS}_2 \) [56, 57], there is no band gap between acoustic branches and optical branches. All the rest of vibrational branches along other lines in BZ are non-degeneracy, except the vibrational branches along R–X line at the boundary of BZ, which are two order degeneracy. The lifting of degeneracy of vibrational branches reveals the Piers phase transition from a high symmetric structure. The absence of the imaginary frequency throughout the 2D BZ indicates the structural stability of the \( T'\text{-MoS}_2 \). Our results are in good agreement with those obtained in [24].

3.4.2. Symmetric analysis of lattice vibrational modes. Both laser Raman (R) scattering and infrared (IR) absorption spectra are powerful tools for structural identification and characterization of 2D materials. To guide the optical spectra study in future experiments, we deduce the symmetry classification of phonon modes at the \( \Gamma \) point by using group theory, and further point out R and IR activity of the optical modes. The unit cell of \( T'\text{-MoS}_2 \) consists of two S-Mo-S units with a total of six atoms, suggesting that there are eighteen phonon modes (three acoustic and fifteen optical modes) at the \( \Gamma \) point. Lattice vibrations can be classified based on the irreducible representation of the space group [58]. The space group of \( T'\text{-MoS}_2 \) is \( C_{2h}^2 \) (or \( P2_1/m \), No.11), whose factor group is isomorphic with the point group \( C_{2h} \). The character table for point group \( C_{2h} \) is given in table 1, where \( A_g \), \( A_u \), \( B_g \) and \( B_u \) are signs of one-dimensional irreducible representations; \( A \) and \( B \) are used when the character of the major rotation operation is 1 or \(-1\), respectively; the subscripts g(gerade) and u(ungerade) denote representations that are symmetric and antisymmetric with respect to the inversion operation if the point group has a center of inversion symmetry; \( x \), \( y \), and \( z \) are components of polar vectors. From table 1, we note that \( T'\text{-MoS}_2 \) has no two-dimensional irreducible representations, i.e. there is no degenerate optical modes at the center of BZ, which distinctively differs from that of \( H \text{- and T-MoS}_2 \) [56, 59–61].
We classify the lattice vibrational modes of T'-MoS2 at Γ by group theory according to the irreducible representations of C2h. Characters of atomic displacement vector representations, primitive cell equivalent representations, and lattice vibration representations of T'-MoS2 are shown in table 2. These representations can be reduced into the irreducible representations summarized in table 1:

\[
\Gamma_{\text{vector}} = 1A_u \oplus 2B_u, \quad (7)
\]

\[
\Gamma_{\text{equivalent}} = 3A_g \oplus 3B_u, \quad (8)
\]

\[
\Gamma_{\text{vibration}} = \Gamma_{\text{equivalent}} \otimes \Gamma_{\text{vector}} = (3A_g \oplus 3B_u) \otimes (1A_u \oplus 2B_u) = 3A_u \oplus 6B_u \oplus 3B_g \oplus 6A_g, \quad (9)
\]

where \(\Gamma_{\text{vector}}, \Gamma_{\text{equivalent}},\) and \(\Gamma_{\text{vibration}}\) are symmetry representations of atomic displacement vector, the equivalent representations of the primitive cell and the symmetry representations of lattice vibration at the zone center of BZ, respectively. The symmetry representation of lattice vibration is equal to the direct product of the symmetry representations of the atomic displacement vector and the equivalent representations of the primitive cell [58].

This symmetry representation of lattice vibration includes eighteen phonon modes in total and can be further decomposed into the representations of acoustic and optical modes as follows:

\[
\Gamma_{\text{acoustic}} = A_u \oplus 2B_u, \quad (10)
\]

\[
\Gamma_{\text{optical}} = 2A_u \oplus 4B_u \oplus 6A_g \oplus 3B_g, \quad (11)
\]

where the acoustic modes include one \(A_u\) and two \(B_u\) modes, all their frequencies are identical to zero; the rest of the fifteen nonzero frequency modes belong to optical modes. The six optical modes of odd parity \((2A_u\) and \(4B_u)\) are IR active, the other nine optical modes of even parity \((6A_g\) and \(3B_g)\) are R active. The R and IR modes are mutually exclusive in T'-MoS2 phase because of the presence of inversion symmetry in the crystal. It is also worth pointing out that the above symmetry analyses is suitable for all T' phase of 2D TMD, namely, T'-MX2 with \(M = (Mo, W)\) and \(X = (S, Se, \text{and Te})\). For easy identifying T'-MoS2 from a Raman optical spectral experiment, we compare the R modes of T'-MoS2 with those of H- and T-MoS2 [60, 61]. It can be found that both H and T phase of MoS2 have two-dimensional \(E'(1)\) and \(E_2\) modes, while T' phase has only one-dimensional modes, no two-dimensional \(E\) mode. This means that if one detects the \(E\) mode in a Raman optical spectral experiment on a MoS2 monolayer, it could not be in T' phase. In addition, since the presence of inversion symmetry both in atomic structures of T- and T'-MoS2, according to exclusion principle, the R modes in these two phase must be g modes, where T phase has both one- and two-dimensional g modes \((A_g\) and \(E_g)\) but T' phase has only one-dimensional g modes \((A_g\) and \(B_g)\). In H-MoS2, however, there is no inversion symmetry and thus no g or u mode. Therefore, we may draw the conclusion that if one finds some one-dimensional but no two-dimensional R modes of g symmetry in a Raman optical spectral experiment on a MoS2 monolayer, then this MoS2 monolayer is probable in T' phase.

### Table 1. Character table for the point group C2h including basis functions of the irreducible representations.

| SG  | PG  | E  | \(C_2\) | \(\sigma\) | i  | basis                      |
|-----|-----|----|---------|-----------|----|---------------------------|
| \(\Gamma_1^-\) | \(A_g\) | 1  | 1       | 1         | 1  | \(R_x, x^2, y^2, z^2, xy\) |
| \(\Gamma_1^+\) | \(B_g\) | 1  | -1      | -1        | 1  | \(R_y, Rx, yz, yz\)      |
| \(\Gamma_2^-\) | \(A_u\) | 1  | 1       | -1        | -1 | \(z\)         |
| \(\Gamma_2^+\) | \(B_u\) | 1  | -1      | 1         | -1 | \(x, y\)      |

We classify the lattice vibrational modes of T'-MoS2 at Γ by group theory according to the irreducible representations of C2h. Characters of atomic displacement vector representations, primitive cell equivalent representations, and lattice vibration representations of T'-MoS2 are shown in table 2. These representations can be reduced into the irreducible representations summarized in table 1:

Table 2. Characters of vector, equivalent, and vibration representations for T'-MoS2.

| \(\chi_{\text{vector}}\) | \(\chi_{\text{equivalent}}\) | \(\chi_{\text{vibration}}\) |
|-------------------------|-------------------------------|-----------------------------|
| 3                       | 0, 6                          | 0, 6                        |
| 1                       |                               |                             |

### Table 3. Classification of the fifteen optical modes in T'-MoS2 according to irreducible representations and optical activity, where the optical modes are denoted by bold Arabic number from 4 to 18 and their frequencies are given in parentheses in the unit of cm\(^{-1}\).

| Raman modes | Infrared modes |
|-------------|----------------|
| \(A_u\)     | \(B_u\)       |
| 5(143.267)  | 4(138.905)    |
| 6(206.684)  | 7(207.684)    |
| 13(276.776) | 11(270.917)   |
| 14(314.290) | 18(451.503)   |
| 15(377.570) | 17(398.414)   |

3.4.3. Eigenfrequency and eigenvector of optical modes. For comparing quantitatively with optical spectra experiments, we compute the eigenfrequency of the fifteen optical modes by Phonopy. In table 3, the fifteen optical modes with frequency are grouped by their irreducible representations and optical activity, where the bold Arabic numbers represent the optical modes, whose ordering is according to their frequencies from low to high. T'-MoS2 structure can be identified and characterized based on table 3 in future optical spectra experiments. Besides, the vibrational eigenvector of the IR and R modes are also illustrated in figures 9 and 10. For IR modes, as can be seen in figure 9, both the two \(A_u\) modes 8(210.225) and 12(271.867) are vibrating along the in-plane directions, while only one \(B_u\) mode 18(451.503) is of the highest frequency, vibrates perpendicular to crystal plane. For IR modes, from figure 10 we find that all the three \(B_u\) modes 4(138.905), 7(207.684) and 11(270.917) are in-plane vibrations, while none of the six \(A_g\) modes are vibrating along purely the in-plane or out-plane direction. The vibration direction of IR and R active modes is vital for setting the incident and detection directions as well as the polarization of the light used in the optical spectra experiments.
3.5. The electronic band gap of T'-MoS2

There has been a discrepancy about the band gap of T'-MoS2 presented in recent literature [7, 24, 27]. Kan et al performed spin-polarized DFT calculations with GGA-PBE and with HSE06 to investigate the band structure of monolayer of T'-MoS2. They pointed out that the structural distortions of ZT-MoS2 lead to the opening of a direct gap of 0.022 or 0.23 eV. The band gap obtained by DFT with GGA-PBE is significantly different from that obtained with HSE06, the latter is ten times greater than the former [7]. Qian et al later found that 1T'-MoS2 (i.e. T'-MoS2) was a semiconductor with a band gap of 0.1 eV based on a many-body perturbation theory within the GW approximation [24]. However, Gao et al’s calculation by DFT based on Dmol3 software showed that T'-MoS2 was a semiconductor with a very narrow band gap of 0.006 eV [27]. Generally speaking, the band gap is underestimated by GGA-PBE, but overestimated by HSE06. Thus, the band gap of 0.1 eV obtained by Qian et al [24] should be closer to the real value since this value is in between the two results: 0.022 eV and 0.23 eV, where the former is calculated by DFT with GGA-PBE and the latter is with HSE06. As to the band gap of 0.006 eV [27], it may seriously underestimate the band gap since it is far lower than the underestimated result 0.022 eV. To examine our inference, we calculate the electronic band structure of T'-MoS2 by DFT with GGA-PBE to explore the effect of spin–orbit coupling. Figure 11 shows the electronic band structure of T'-MoS2 before (a) and after (b) considering spin–orbit coupling. The vacuum level is set to zero. The band gap is opened by spin–orbit coupling.
Figure 12. Orbital-projected fine band structures of (a) Mo and (b) S atoms around the Γ point without considering spin–orbit coupling. The diameter of circle indicates the weight of components.

In general, but the crucial difference in detail occurs near the Fermi line. In the former case, there seems to be no band gap, while in the latter case, the band gap does present, and is equal to 0.048 eV. This result implies that it is the spin–orbit coupling that opens or widens out the band gap. Besides, we also find that the band structure without considering the spin–orbit agrees well with that of Gao et al’s especially in the vicinity of the Fermi line.

To determine whether there exists a very small band gap without spin orbital interaction, we plot the orbital-projected band structures [62] of Mo and S atom around the Γ point without considering spin–orbit coupling. As can be seen in figure 12, for both Mo and S atom, the two bands meeting at the Fermi line cross each other directly without any avoidance. This direct crossing shows that there is exactly no band gap existing in electronic band structure of T’-MoS2, as well as T’-MoS2 with spin-orbit coupling. In addition, we recalculate the electronic band structure of T’-MoS2 by DFT with HSE06 and the obtained band gap is about 0.153 eV, which falls in between those obtained in [7] and [24]. Thus far, we can come to conclusion that T’-MoS2 must be a semiconductor of a narrow gap, while Gao et al’s calculation may have not included the spin–orbit interaction.

4. Conclusions

In conclusion, we have performed first-principles investigation on the structure, physical stability, optical modes and electronic band gap of T’-MoS2. Our simulated STM images of MoS2 monolayer are in good agreement with previous experimental results. Moreover, we have found unexpectedly that the simulated STM images of T’-MoS2 vary significantly with the scanning distance. This variation should be considered in the structural identification from experimental STM images. Furthermore, the dramatic similarity between the simulated STM images of T’-MoS2 with that of earlier experimental study means that T’-MoS2 may have been observed in experiment, but was mistaken for the intercalation compound Kx(H2O)yMoS2. If so, T’-MoS2 should be stable in structure. To verify its physical stability, the thermal and mechanical stability of T’-MoS2 have been explored by AIMD simulations and elastic constants fitting and the results are affirmative. In addition, the lattice dynamic stability of T’-MoS2 is also confirmed by the absence of an imaginary frequency in our phonon dispersions relations. Therefore, the physical stability of T’-MoS2 has been verified finally. Besides, we have made symmetry classification of optical modes and calculated their eigenfrequencies and eigenvectors, which provides an important guidance for further optical spectral study in experiments. Future work will investigate the intensity of R and IR spectra theoretically.

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