

===== MATHEMATICAL MODELING =====

Modeling the properties of 2D-materials hybrid nanostructures coupled with ferroelectric polymer PVDF

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Abstract. Transition metal dichalcogenide (TMD) monolayers are very promising for many applications, as well as graphene and hexagonal nitride boron layers (h-BN), especially in the fields of optics as emitters and detectors, in electronics as transistors. It is first of all due to the fact that they have a direct band gap E_g , which is dependent on external applied electric fields. To create such an electric field, it is proposed to use the field induced polarization of ferroelectric polymer layer such as polyvinylidene fluoride (PVDF) and poly(vinylidene fluoride-trifluoroethylene) P(VDF-TrFE). These polymers in the ferroelectric phase can create significant polarization in very thin layers, about 5 Å. By combining such ferroelectric layers and TMD layers, hybrid nanostructures can be created, that are convenient for design of new photodetectors with controlled properties. The outstanding properties of this hybrid structure are due, in particular, to the ultra-high electric field induced by ferroelectric polarization in PVDF or P(VDF-TrFE), which acts on the TMD layers and regulates the band gap E_g . In this work, we simulate such a hybrid structure based on PVDF and MoTe₂, h-BN, graphene layers and study their features and properties. To calculate all the main properties, density functional theory (DFT) methods implemented in the Quantum ESPRESSO program are used. Semi-empirical PM3 method implemented in the HyperChem software package are used to model and study both individual layers of the hybrid structure and the features of their joint interaction, as well as to study vibration modes. The results obtained convincingly demonstrate a strong influence on the width of the band gap E_g and vibration modes frequencies of all the studied nanostructures due to the influence of the ferroelectric polarization P and the polarization-induced electric field E , which affects all the layers of the hybrid heterostructure.

Key words: *density functional theory, dichalcogenides, graphene, nitride boron, band gap, vibration modes, polymer ferroelectrics, heterostructure*

1 INTRODUCTION

Low-dimensional and layered 2D-dimensional nanomaterials are increasingly attracting the attention of researchers studying their properties and are finding an increasingly diverse range of diverse applications. The emergence of graphene has demonstrated remarkable properties that have prompted the search for many other new 2D-dimensional materials and van-der-Waals nanostructures [1–6]. Today, numerous 2D-materials exist worldwide, such as transition metal dichalcogenides (TMD, such as MoS₂, MoTe₂, WS₂, etc.) [7–12] and other new systems, offering a variety of promising applications in electronics, optics, sensors, and other fields. For example, TMDs are among the most studied 2D-semiconductors for use in the electronics, optoelectronics, spintronics, and memory devices. Very popular and attractive for many applications are 2D-materials such as 2D-semiconductors with narrow band gaps:

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platinum diselenide (PtSe₂) [13], hexagonal boron nitride h-BN [14, 15], black phosphorus [16], black arsenic phosphorus [17], and graphene in its various modifications [3, 18].

Among the many applications of 2D-materials, one important and promising area is their use in the fabrication of various photodetectors. Depending on the type of 2D-material, it is possible to create detectors for various electromagnetic wave ranges – from the ultraviolet (UV) and visible optical range to the long-wave infrared (LWIR) range. Here, transition metal dichalcogenides (TMDs) represent an important class of two-dimensional materials; they offer enormous potential for applications in various photodetectors due to their excellent optoelectronic properties [10–12]. It is also important that many of them are well suited for detecting infrared radiation and waves, particularly the LWIR range. This LWIR range is important for many applications, particularly in thermal imaging.

Not only is it crucial to determine the intensity of incident waves, but also to detect and extract information about the polarization of the incident wave. Information about the polarization of light is even more crucial in medical applications, remote sensing, and, especially, in infrared polarization photodetection. The development of polarization detection technology in the long-wavelength infrared range has significant implications, including transforming traditional thermal imaging into identification imaging, improving target identification capabilities, and protecting against interference, which is essential in fields such as medicine, information transmission and communications, space exploration, industrial quality control, and environmental monitoring.

Currently, there are no well-developed detection technologies with very high polarization sensitivity in the long-wavelength infrared range, which covers a wavelength range of 8–14 μm ($\sim 0.177\text{--}0.089$ eV). Low-dimensional materials demonstrate big potential in high-efficiency polarization photodetectors, which corresponds to the current trend toward miniaturization and high integration for next-generation on-chip optoelectronic devices [19]. A promising direction in this area, for example, may be the approach proposed in [20].

However, here, first and foremost, it is necessary to study and understand the physical mechanisms of optical and infrared wave detection and intensity detection with high sensitivity in photodetectors based on 2D-materials and TMDs. Despite active development, these infrared detectors typically have low photocurrent gain and quantum efficiency due to limited absorption efficiency, the presence of dark currents, etc.

These shortcomings can be overcome by influencing the properties of 2D-nanostructures with other materials, such as ferroelectric polarization layers, which create an internal electric field in joint combined heterostructures. For example, a ferroelectric polymer [21] such as polyvinylidene fluoride (PVDF) or poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) [22, 23] can be used. These materials are formed as 2D-dimensional ferroelectric layers of the Langmuir-Blodgett films [22, 23] or using spin-coating method [24] and incorporated into the heterostructures along with the TMD layers.

In this case, their polarization-induced electric field influences the electronic and optical properties of the TMD layers, altering the band gap and influencing the photocurrent. Here, it is necessary to thoroughly understand the possibilities of such control and regulation of the boundaries, width, and intensity of the signal recorded by the photosensor using this electric field, which arises from the polarization of the ferroelectric layer embedded in the overall heterostructure of the device.

This was first experimentally demonstrated, for example, in [25], and then developed further in [26–28], including on 2D structures of various TMD layers (MoTe₂, ReS₂, etc.). These devices demonstrate ultrasensitive and highly efficient characteristics and allow for control over the properties of TMD structures [29, 30]. In particular, such a photodetector, built on a hybrid heterostructure composed of a layer of organic polymer ferroelectric (P(VDF-TrFE)) with molybdenum disulfide (MoS₂), offers significant advantages in recording a tunable and broader infrared range [25]. The sensitivity of the device in this spectral range is significantly increased. Moreover, the electric field of ferroelectric

polarization significantly enhances the photoconductive properties of MoS₂ and suppresses dark current and noise.

This approach represents a reliable path to creating highly efficient photodetectors with a remarkably wide spectral response range, high sensitivity, low power consumption, and the ability to operate at room temperature. These excellent optoelectronic properties are due to the combination of multiple mechanisms in ferroelectric materials and two-dimensional semiconductors, such as pyroelectricity, ferroelectricity, and photoconductivity, in a single device. The most impressive characteristic of this type of detector is the synergistic nature of all these mechanisms.

For a detailed development of possible designs of such multicomponent complex heterostructures, incorporating active control ferroelectric layers, it is necessary to study the individual layer components and their interactions.

This can be effectively accomplished using computer modeling of the corresponding structural components and quantum calculations of their physical properties and interaction features. We applied this approach, using the example of the interaction between graphene and PVDF layers, in [31–36]. Semi-empirical quantum chemical methods were used in [37] to study the interaction model of a TMD such as MoS₂ with a PVDF ferroelectric layer. Similarly, but using more advanced quantum calculation methods, such as density functional theory (DFT), we can also consider modeling the interaction of other TMDs with polymer ferroelectric layers. In this paper, we consider the modeling of a number of such structures: MoTe₂, h-BN, Graphene, and their interaction with a PVDF layer.

2 BASIC METHODS AND CALCULATION DETAILS

All our calculations were performed using density functional theory (DFT) within the Kohn-Sham formalism [38–41] in combination with semi-empirical methods of quantum chemical calculations [42–45] in the Hartree–Fock (HF) self-consistent field (SCF) approach. For DFT calculations of graphene, MoTe₂, and h-BN nanostructures based on carbon (C), molybdenum (Mo), tellurium (Te), nitrogen (N), and boron (B), ultrasoft pseudopotentials were used [46]. These are sufficient if we are interested in calculating only the geometry (and its variations) and the energy band structure. Ultrasoft pseudopotentials (USPs) were introduced by Vanderbilt (1990) [46] to allow calculations with the lowest possible cutoff energy for a plane wave basis set. The computational DFT methodology uses the Perdue, Burke, Ernzerhof (PBE) functional with a generalized gradient approximation (GGA) [47]. All DFT calculation with this functional were performed using the Quantum ESPRESSO package [48].

Kinetic energy thresholds were set at 50 and 700 Ry for the Kohn–Sham wave functions and the semi-local potential. The forces acting on the atoms were estimated based on the calculated ground-state electronic structure. The search for a stable atomic configuration was performed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [49, 50] for numerical optimization of the total energy. For the DFT calculations of the layered structures of MoTe₂, h-BN and Graphene, an automatic k -point sampling mesh (K_POINTS) with a mesh dimension and shift of $k_1 \times k_2 \times k_3$ was used, which was different for each modelled periodic structure.

The next main tool for molecular modelling of all studied nanostructures in this work was the HyperChem 8.01 software package [51] with semi-empirical method PM3 [41–44] in the restricted Hartree–Fock (RHF) approximation for calculation of the isolated atomic cluster in the limited volume. Optimization of molecular systems and the search for their optimal geometry is carried out in this work using the Polak–Ribeire algorithm (conjugate gradient method), which determines the optimized geometry at the point of their minimum total energy [51]. For such optimized structures, dipole moments D and electronic energy levels (such as E_{HOMO} and E_{LUMO}), as well as the band gap $E_g = E_{\text{LUMO}} - E_{\text{HOMO}}$, were then calculated using Single-Point (SP) method. For each optimized molecular structure, the volume V was

calculated using the QSAR program implemented in the HyperChem software package [51]. This then allows one to determine the polarization P of the studied structure, since the polarization $P \sim D/V$ is the dipole moment D per unit volume V of the structure.

Furthermore, the system was simulated and all its key parameters were calculated under a simulated applied constant electric field, which is also available in the HyperChem packages [51]. Determining the fundamental vibrational modes of the modeled layered structures is also important—these calculations were performed using a special option in the HyperChem program built into "Vibration, Rotation analysis" [51]. The initial structural data for the MoTe_2 , h-BN, and graphene were obtained from the Cambridge Crystallographic Data Centre1 (CCDC) crystallographic database [52] and from a number of relevant publications. Based on these data, crystallographic cell models were constructed and calculated using density functional theory (DFT) methods in the Quantum ESPRESSO program [49]. For molecular modeling and quantum chemical calculations, as well as vibrational analysis, these models were transferred to the HyperChem workspace [51].

3 MAIN RESULTS AND DISCUSSION

3.1 Modelling and computational data for MoTe_2 structure

MoTe_2 is a layered transition metal dichalcogenide (TMD) with a sandwich structure (Te-Mo-Te) held by Van der Waals forces [53]. Each layer consists of a hexagonal close-packed plane of Molybdenum (Mo) atoms sandwiched between two planes of Tellurium (Te) atoms. Strong intralayer covalent bonds and weak interlayer Van der Waals forces ensure easy exfoliation. MoTe_2 exhibits phase polymorphism [54] – it exists in three main phases: the semiconducting 2H (hexagonal) phase, the semimetallic 1T' (monoclinic) phase, and the orthorhombic phase. The 2H phase is most stable at room temperature. We consider mainly this phase state in our work here.

In our calculations the primitive cell of single-layer MoTe_2 containing one Mo atom and two Te atoms was used under periodic boundary conditions. To avoid possible periodic interactions, a vacuum space of 20 Å was used, located along the z axis. The valence electrons $s2p4$ for Te and $4p5s4d$ for Mo were included in the PAW pseudopotentials. For single layer MoTe_2 calculation (with a direct band gap) PBE-GGA method was used [47]. For the self-consistent calculations, the Brillouin zone (BZ) was sampled by $8 \times 8 \times 1$ Gamma-centred k -point grid obtained with Monkhorst-Pack scheme for Quantum ESPRESSO calculation [48]. Experimental data for MoTe_2 (Space group $P6_3/mmc$ (No. 194)) is taken from [53]: $a = 3.5182$ Å, $b = 3.5182$ Å, $c = 13.9736$ Å; when the cell size along the z -axis increases to $c = 20$ Å, (Space group $P1$ (No. 1)). For a hexagonal structure, the cell angles are: $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$.

Figure 1 shows models of a MoTe_2 monolayer with several unit cells of a periodic structure in different projections (Figs. 1a, 1b, 1c), as well as similar MoTe_2 structures, constructed in the working space of the HyperChem (Fig. 1d, 1e, 1f). The inset (1g) shows the unit cell of the MoTe_2 .

The results of the energy calculations performed using Quantum ESPRESSO [47, 48] are shown in Figure 2, corresponding to the monolayer MoTe_2 (Fig. 1a, 1b). The minimal value of the energy gap obtained from this calculation $E_g = 1.1312$ eV ~ 1.13 eV at the K point (Fig. 2a) is close to the data from work [55] (Fig. 2b), as well as to the value of the direct transfer $E_g \sim 1.1$ eV from [56].

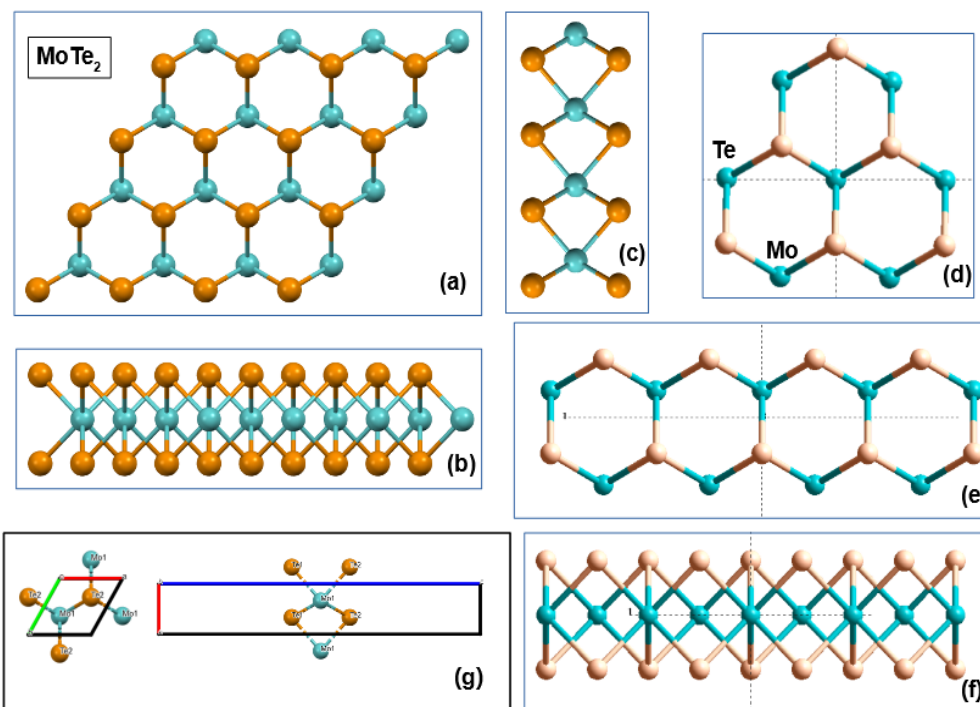


Fig. 1. Models of a MoTe₂ monolayer with several unit cells of the periodic structure and models of atomic clusters constructed in the HyperChem working space in different projections: **a)** top c-view, **b)** side b-view, **c)** side c-view; **d)** top view of 19-atoms-model – MT-19, **e)** top view of 27-atoms-model – MT-27, **f)** side view of 27-atoms-model – MT-27. The inset **g** shows the minimum unit cell of the MoTe₂

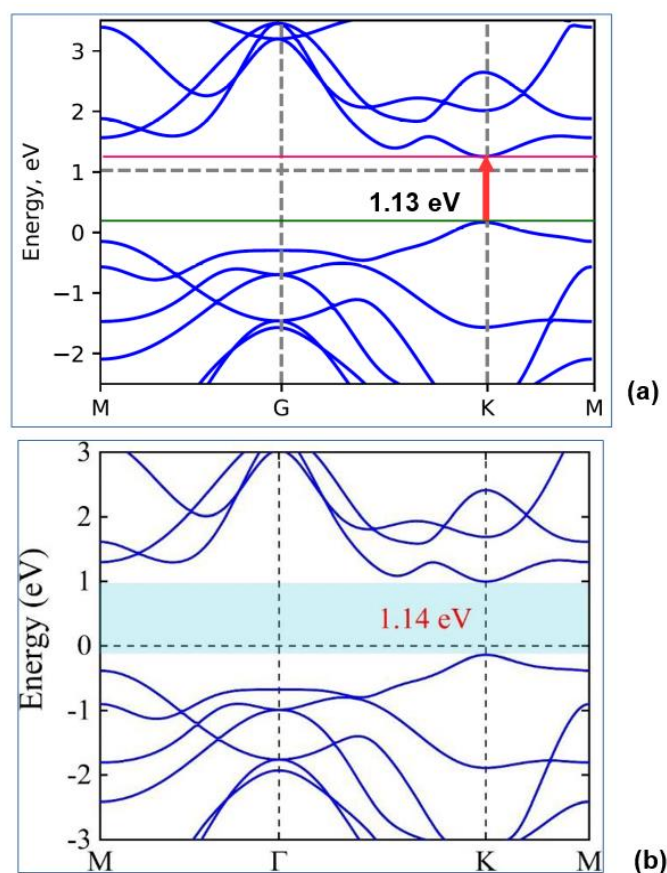


Fig. 2. The energy band structure of MoTe₂ calculated using the Quantum ESPRESSO program **(a)** compared with data **(b)** from [55]

The lattice constant a , obtained in our DFT calculation from self-consistent GGA-PBE approach, ($a = \sim 3.554955 \text{ \AA} = \sim 3.555 \text{ \AA}$) is close to the known data $a = \sim 3.519 \text{ \AA}$ [57, 58]. In the MoTe_2 structure, each Me is coordinated to a trigonal prism of six telluriums; the Mo-Te distance is $\sim 2.73 \text{ \AA}$ [57]. We obtained close data for this distance $\sim 0.279 \text{ nm} = \sim 2.79 \text{ \AA}$.

To study the properties of layered MoTe_2 structures, which are important for their applications in electric-field-controlled infrared detectors (and especially, in the LWIR range), it is first necessary to study their vibrational properties, determine their fundamental vibrational modes, and evaluate their possible dependence on the applied electric field. It is also important to evaluate the change in the band gap width of E_g with the electric field intensity E . To study the vibrational modes in this work, we used the HyperChem program, which has a built-in option for calculating and analysing various vibrational modes: option of the Vibration, Rotation Analysis [51].

To perform these calculations, atomistic cluster models of MoTe_2 layered structures were constructed in the HyperChem working space (Fig. 1d, e, f), and the main quantum chemical calculations of the energy and dipole parameters were performed in the semi-empirical restricted Hartree-Fock (RHF) approximation PM3 [42–44]. The main results are presented in Table 1.

Calculating the vibrational modes on these models in the HyperChem program allowed us to obtain the spectra of the fundamental vibrations of the MoTe_2 layers. Examples of the spectra are shown in Figure 3. The fundamental modes are also listed in Table 1.

Table 1. Computed data of MoTe_2 models (at $E_z = 0$) by PM3 RHF method

	E_{HOMO} , eV	E_{LUMO} , eV	E_g , eV	D_z , Debye	D_y , Debye	D_x , Debye	ν_1 , cm^{-1}	ν_2 , cm^{-1}	ν_3 , cm^{-1}	ν_4 , cm^{-1}
MT-19	-7.3503	-3.4413	3.9091	0.014	5.247	5.247	29	93	170	296
MT-27	-7.1454	-3.2478	3.8976	0.015	9.689	9.799	18.6	81	167	289
from [59]							0–40	40–150	150–200	200–300

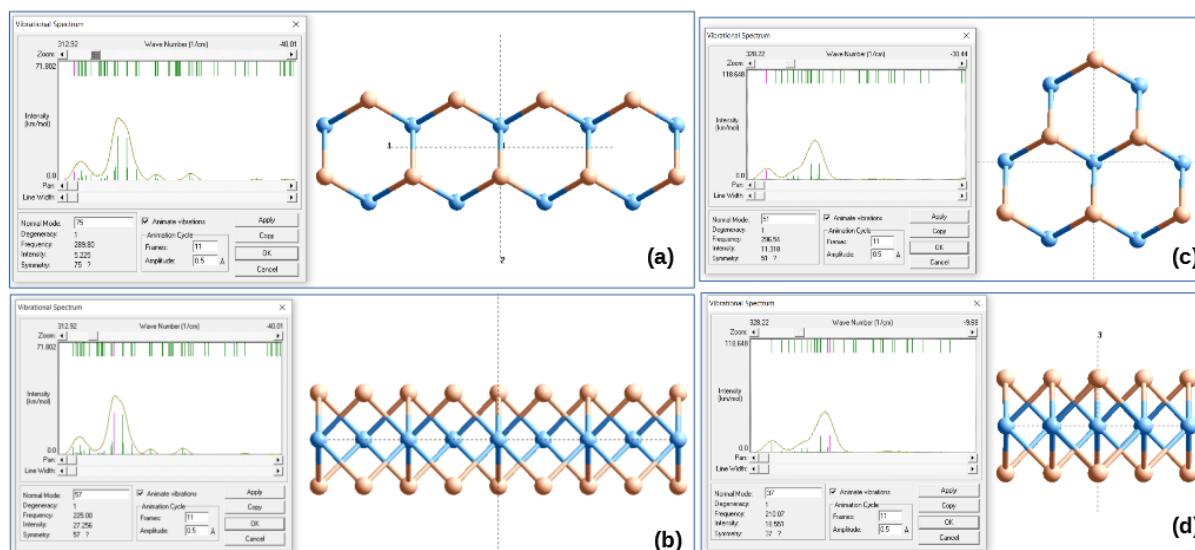


Fig. 3. Examples of Vibrational spectra for MoTe_2 models structures: **a)** top c-view of MT-27 model, **b)** side b-view of MT-27 model, **c)** top c-view of MT-19 model, **d)** side b-view of MT-19 model

The obtained vibrational mode spectra are consistent with data from other authors [59, 60]. Layered MoTe_2 structure exhibits several main vibration modes, which were studied

by various methods, including distinct Raman-active vibrational modes spectroscopy, primarily divided into high-frequency intralayer ($\sim 200\text{--}300\text{ cm}^{-1}$) and low-frequency interlayer ($< 40\text{ cm}^{-1}$) modes [59, 60]. Key modes include the out-of-plane, in-plane, and layer-dependent shear (S) and breathing (LB) modes. Moreover, as visual observation in the "motion animation" mode in the HyperChem workspace shows, high-frequency oscillations are associated predominantly with the motion of Mo atoms, while the low-frequency oscillations are due to the more active motion of Te atoms. It should also be noted that these oscillation frequency ranges are ($200\text{--}300\text{ cm}^{-1}$), ($40\text{--}200\text{ cm}^{-1}$) and less than 40 cm^{-1} correspond to values of ($50\text{--}33\text{ }\mu\text{m}$), ($250\text{--}50\text{ }\mu\text{m}$), and greater than $250\text{ }\mu\text{m}$, which refers to the infrared (IR) ranges in the very long-wave infrared (VLWIR) subrange: $15\text{--}1000\text{ }\mu\text{m}$. IR radiation detection in this range is carried out using sensors of the appropriate types.

In this paper, we are further interested in how these key modes might respond to the action of an external electric field. To reveal this effect, we further perform similar calculations and analyse the changes in E_g and the fundamental vibrational frequencies depending on the applied electric field intensity. Table 2 shows the main results obtained for the MT-27 model of MoTe_2 .

It should be noted that in this case, as can be seen, the value of E_g for the initial layered structure in the HyperChem models differs from the result obtained in the DFT calculations. This is due to the fact that a cluster model in a limited volume is considered here, rather than a periodic structure. In principle, these values are similar. But, for the aim of our study it is important to evaluate the relative change of the E_g with the applied electric field E , as well as the key vibrational modes changes.

Table 2. Dependence of the electron energy levels for MoTe_2 (model MT-27) and key vibration modes from the electric field E_z , computed using PM3 RHF method (HyperChem)

E_z , V/nm	E_{HOMO} , eV	E_{LUMO} , eV	E_g , eV	D_z , Debye	D_y , Debye	D_x , Debye	ν_1 , cm^{-1}	ν_2 , cm^{-1}	ν_3 , cm^{-1}	ν_4 , cm^{-1}
−8.75	−7.1075	−3.1127	3.9948	32.199	9.204	33.508	17	52	161	285
−7.5	−7.1209	−3.1428	3.9782	27.273	9.307	29.273	20	53	161	285
−5	−7.1304	−3.1941	3.9363	18.732	9.465	21.035	25	53	170	298
−3.75	−7.1365	−3.2159	3.9206	14.116	9.524	17.076	28	56	166	288
0	−7.1454	−3.2478	3.8976	0.015	9.689	9.799	18.6	81	167	289
3.75	−7.1365	−3.2164	3.9202	−14.099	9.530	17.078	27	101	190	311
5	−7.0990	−3.1868	3.9362	−18.860	9.739	21.237	19	105	198	310
6.25	−7.1293	−3.1710	3.9583	−23.223	9.355	25.069	25	105	193	309
9	−7.1121	−3.1097	4.002	−33.042	9.150	34.308	34	106	195	316
$\text{MoTe}_2\text{+PVDF}$	−6.4262	−2.5338	3.8924 ^{*)}	18.222	12.484	22.089				
$\text{MoTe}_2\text{+rPVDF}$	−7.5906	−3.5192	4.0715 ^{**)}	−10.119	10.242	14.404				

A graphical representation of the behavior of E_g with the applied field E_z is shown in Figure 4. Figure 5 also shows the behavior of the key vibrational modes of the MoTe_2 (MT-27 model) with varying external electric field E_z .

As can be seen from the obtained calculation results, the electric field has a significant effect on both the band gap E_g (which is important for electronic excitations and optical properties) and the vibrational modes (which is important for structural excitations in the infrared spectral range). In studies on proposed photoelectric and infrared detectors based on 2D layered structures, the design of such a detector (built as a hybrid heterostructure) also utilizes ferroelectric layers such as PVDF or PVDF-TrFE [25–30].

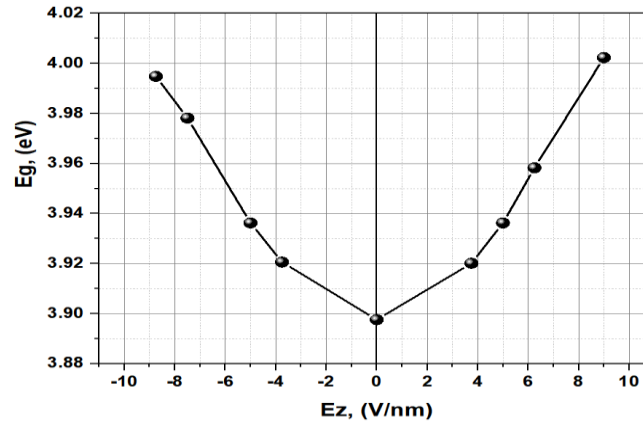


Fig. 4. Dependence of the energy band gap E_g from the applied electric field E_z for MoTe₂ (MT-27 model)

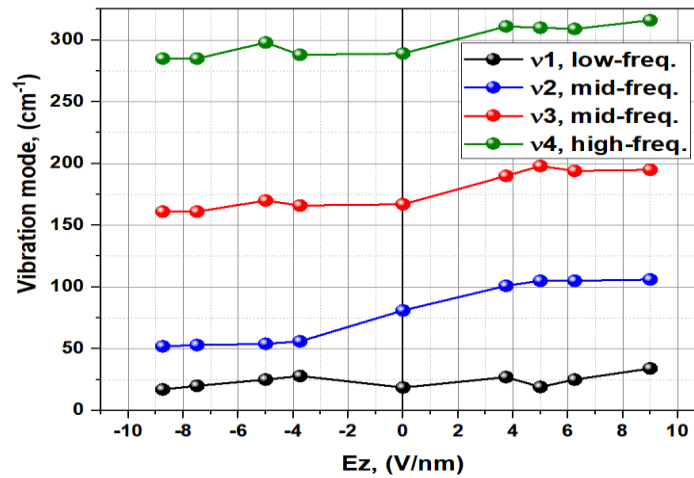


Fig. 5. Dependence of the main vibration modes from the applied electric field E_z for MoTe₂ (MT-27 model)

This is done precisely because the ferroelectric layer has its own polarization, which creates an electric field acting on the 2D-layers of dichalcogenides (TMD, such as MoTe₂, etc.) or other 2D-materials. Here, we will evaluate the possible electric fields arising from the polarization of a ferroelectric using the PVDF chain model shown in Figure 6.

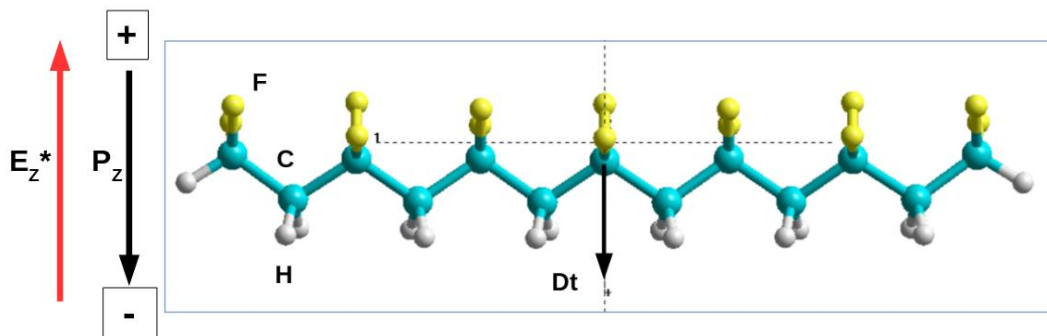


Fig. 6. Model of a chain of polymer ferroelectric polyvinylidene fluoride (PVDF), creating a dipole moment $D_t \sim D_z$, polarization P_z , and a corresponding electric field E_z^* in the surrounding medium

The polarization P is typically obtained from the dipole moment (in Debye units) [31–37]:

$$P = 3.33556255 \cdot D / V \text{ (in C/m}^2\text{)}, \quad (1)$$

where V is structure's volume on the Van der Waals surface.

The prominent physical and electrical properties of this hybrid structure PVDF+MoTe₂ (as well as in another similar 2D-layered structure) arise and benefit from the ferroelectric-polarization-induced ultra-high electric field of the PVDF (or by the P(VDF-TrFE) film as in real usual samples). To determine and estimate the magnitude of this local electric field E_Z^* at the interface between PVDF and MoTe₂ layers, which is created inside the MoTe₂ layer from ferroelectric PVDF polarization with magnitude P , we use the relation

$$E_Z^* = P_Z / (2\epsilon\epsilon_0). \quad (2)$$

Here ϵ is the dielectric constant (permittivity) of the material (for MoTe₂ $\epsilon = \sim 10$ – 12 [61], ϵ_0 is the vacuum constant ($\epsilon_0 = 8.85 \cdot 10^{-12}$ C/(V·m)).

For our PVDF chain model, shown in Figure 6, the dipole moment calculated using the PM3 RHF method is $D_t \sim D_Z = \sim 13.73$ Debye, the corresponding volume of this structure along the van der Waals surface is $V = \sim 267.793$ Å³ (calculated by the QSAR program built into HyperChem). The resulting polarization value (according to Formula (1)) is $P = P_Z = \sim 0.1713$ C/m². The corresponding electric field (2) at $\epsilon = 1$ will be $E_Z^* = P_Z / (2\epsilon\epsilon_0) = \sim 9.67$ V/nm ~ 10 V/nm, and taking into account $\epsilon = \sim 10$ for MoTe₂, the value of $E_Z^* = \sim 1$ V/nm.

Considering that in this case, the model represents two layers of nanostructures (a MoTe₂ layer and a PVDF layer) separated by a vacuum layer of thickness z_0 (Figure 7), the value of ϵ here may differ from that in the MoTe₂ layer alone. For example, for PVDF, the value of $\epsilon = \sim 5$ [24, 31–37], then $E_Z^* = \sim 2$ V/nm.

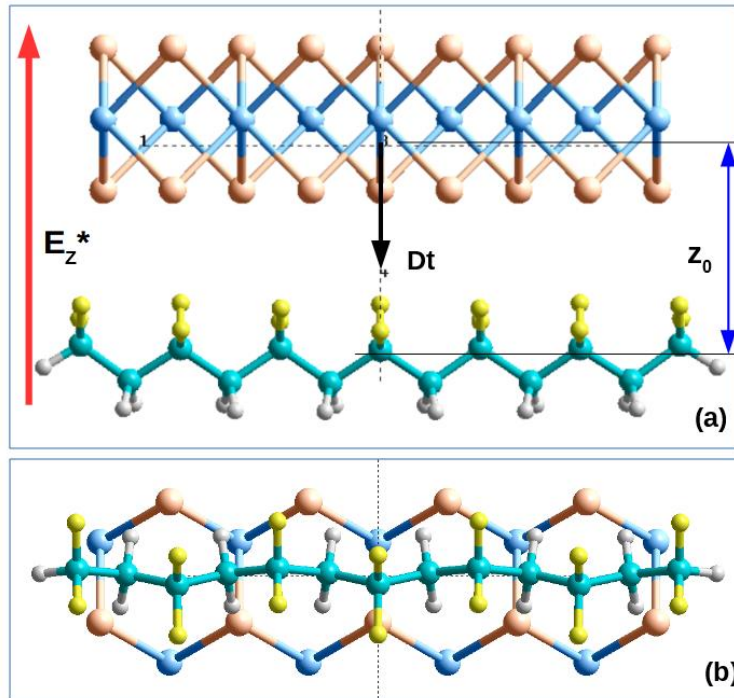


Fig. 7. Model of interacting PVDF and MoTe₂ layers: **a)** view along the OY axis, **b)** top view along the OZ axis

The magnitude of the effective electric field E_Z^* will also depend on the orientation of the dipoles in PVDF and the distance between PVDF and MoTe₂ (as shown in work [37] for similar calculations with MoS₂). For the model in Figure 7, the distance $z_0 = 5.5$ Å, and it can vary. In all these models and calculations, we can only evaluate all the results qualitatively. But in any case, the effective electric field here is on the order of 1–10 V/nm or slightly higher. This can be stated with certainty. As can be clearly seen in Figure 4, variations in the electric field in this range of 1–10 eV/nm significantly alter the value of E_g .

Furthermore, it is also clearly visible in Figure 5 that smooth changes in the fundamental vibrational modes also occur, especially in the middle part of the range. Calculations of vibrational modes in the combined PVDF+MoTe₂ model show the emergence of strong vibrational modes corresponding to PVDF in the various ranges: 2900–3100 cm⁻¹ (for Hydrogen motion), 900–1600 cm⁻¹ (for Carbon motion), 300–600 (for Fluorine motion). From 300 cm⁻¹ start Mo vibration motions, partially mixed with Fluorine motions, up to approximately 160 cm⁻¹, further from 140 cm⁻¹, Te vibrations appear (also partially mixed with fluorine vibrations in the ~ 80 cm⁻¹ region), increasing in the range of ~ (40–10) cm⁻¹.

That is, under PVDF influence, all the fundamental vibrational modes of MoTe₂ remain, but they are partially mixed with PVDF vibrations, are less clearly defined, are somewhat diffuse, and their relative intensity is significantly lower than that of PVDF ones. Since they are difficult to clearly identify here, we do not present their data in Table 2. In the last two rows, we have presented the data on electron energies, E_g^* (marked by *) and **) and dipole moments for such mixed heterostructures as MoTe₂+PVDF (shown in Figure 7, with $z_0 = 5.5$ Å) and MoTe₂+rPVDF (with the PVDF chain flipped or rotated by 180°, which means switching the polarization direction and changing the direction of the electric field). We do not show the drawing of this structure here.

As can be seen, for the case of MoTe₂+PVDF, the value of E_g^* is close to the value of E_g^* at the electric field around $E_Z = 0$ (or close to 1 eV/nm), whereas for the inverted chain in the MoTe₂+rPVDF model, the value of E_g^* corresponds to an electric field greater than $E_Z > 10$ eV/nm.

Thus, it is shown here that the electric field from the polarization of the ferroelectric layer influences and modifies the fundamental frequencies or vibrational modes in the far-infrared range of interest to us. Thus, it is clear that such a PVDF+MoTe₂ heterostructure can form the basis of an adjustable sensor in the far-infrared range, as well as in other ones.

3.2 Modelling and computational data for h-BN structure

Hexagonal boron nitride (h-BN) has a structure similar to graphite and graphene, but its properties are different, making it a versatile material with a wide range of applications. This structure consists of layers of boron and nitrogen atoms linked by strong covalent bonds within each layer [53]. Weaker van der Waals forces hold the layers together. Hexagonal h-BN has a layered structure reminiscent of graphite, with alternating boron and nitrogen atoms. It crystallizes in the P63/mmc space group (no. 194) with the following lattice parameters: $a = b \sim 2.504$ Å, $c \sim 6.656$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$ [53, 62, 63]. The layers (basal planes) are held together by weak van der Waals forces, with the B and N atoms of one layer located above/below the hexagonal centers of adjacent layers (AA' stacking). In hexagonal boron nitride (h-BN), the distance $R(B-N)$ between adjacent boron (B) and nitrogen (N) atoms within a single layer (covalent bonding) is approximately ~ 1.45 Å (0.145 nm) or ~ 1.446 Å [53]. This distance provides a strong structure similar to graphite, while the interlayer distance is significantly larger, which is typical of layered materials and a wide band gap (~ 4.9 eV), density of 2.1–2.3 g/cm³ [62–64].

In our DFT calculations the primitive cell of single-layer h-BN containing one B atom and one N atom was used under periodic boundary conditions with a vacuum space of 20 Å along z-axis. For single layer h-BN calculation (with a direct band gap) PBE-GGA method was used [47]. For the self-consistent calculations the Brillouin zone (BZ) was sampled by a k -point sampling mesh with a mesh dimension and shift of $12 \times 12 \times 1$ for Quantum ESPRESSO calculation [48]. After DFT relaxation of the h-BN monolayer, $a = 2.515$ Å and $R(B-N) = 1.452$ Å were obtained.

Figure 8a, b presents images of the initial h-BH structural data for the DFT calculation based on the cell parameters from [53]. It should be noted here that the distance between the

h-BN planes along the c-axis is increased to 20 Å, as noted above, to avoid possible periodic interactions. The resulting energy band structure is shown in Figure 7c. Below, for comparison, Figure 7d shows the energy band diagram from the work [62].

The narrowest energy gap obtained in our DFT calculations is located at point K and is equal to $E_g \sim 4.70$ eV (Fig. 8c), which is close to the data of $E_g \sim 4.90$ eV from the work [62] (Fig. 8d).

Further in this work, atomistic cluster models of a single h-BN layer are constructed using the HyperChem program [51] in agreement with the structural data for h-BN from [53, 62–64]. Quantum-chemical calculations of all necessary energy quantities and dipole moments were performed in the semi-empirical approximation PM3 RHF also in HyperChem program [51]. Vibrational spectra were calculated in the HyperChem using the Vibration, Rotation Analysis option [51]. Figure 9 shows the corresponding models of a single h-BN layer in comparison with [62].

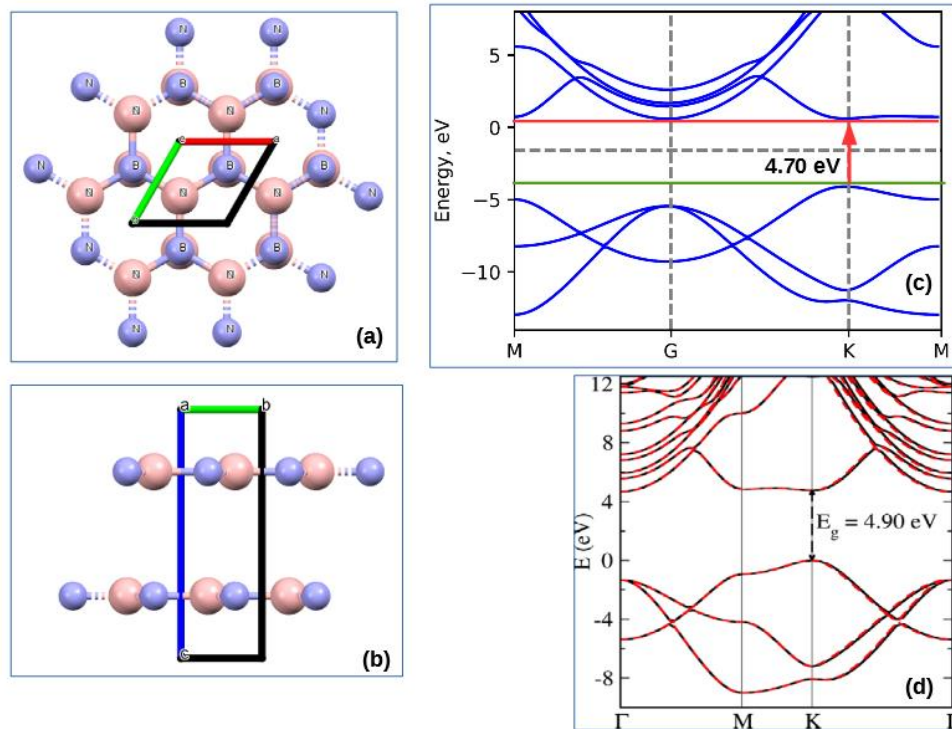


Fig. 8. Models of h-BN periodic layered structure and DFT calculated energy band structure: **a)** top c-view; **b)** side a-view; **c)** calculated energy bands diagram; **d)** energy bands diagram [62]

Table 3 shows the calculated results for the electron energies and fundamental vibrational modes for the h-BN-20 and h-BN-72 models (Fig. 9a, 9b) in the initial state without the influence of an electric field ($E_z = 0$) using the semi empirical PM3 RHF method.

Table 3. Computed data of h-BN models using PM3 RHF method (at zero electric field, $E_z = 0$)

	E_{HOMO} , eV	E_{LUMO} , eV	E_g , eV	D_z , Debye	D_b , Debye	ν_1 , cm^{-1}	ν_2 , cm^{-1}	ν_3 , cm^{-1}
h-BN-20	-7.951	-4.228	3.722	-0.035	4.497	332	700	1265
n-BN-72	-7.927	-4.304	3.622	-0.107	25.011	305	850–880	1320–1360
from [64]						0–600	600–800	1300–1600

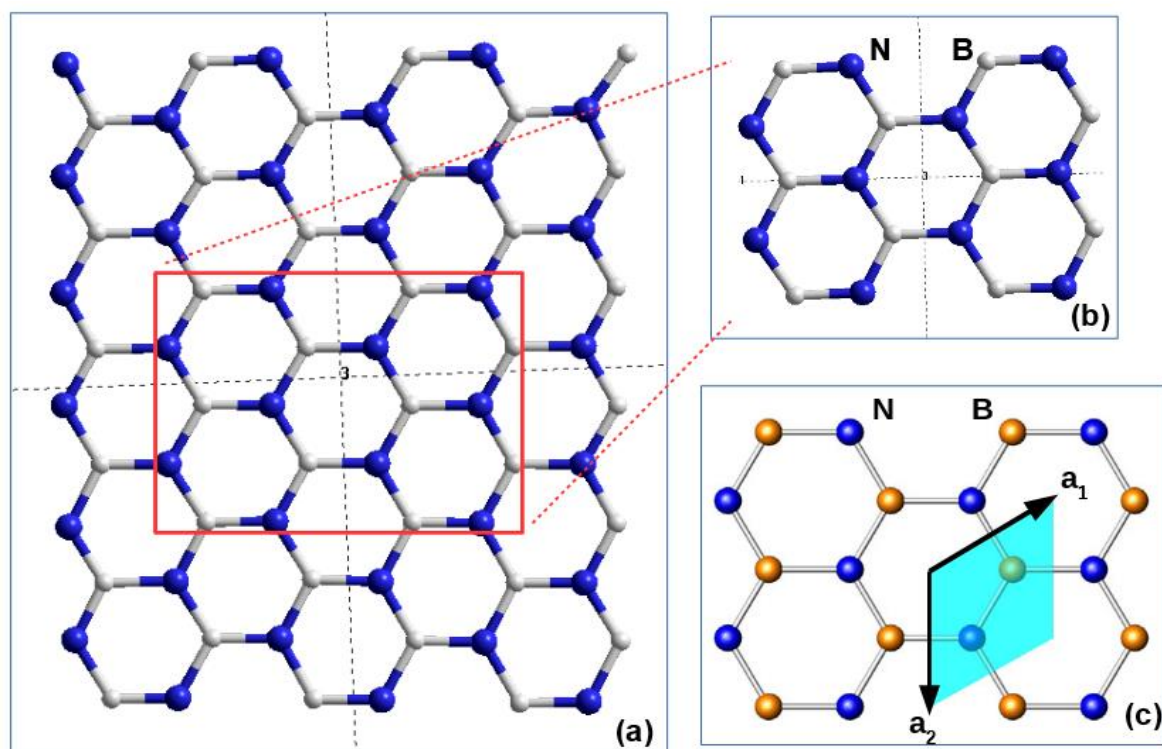


Fig. 9. Model of an h-BN layer structure: **a)** 72-atom h-BN-72 model; **b)** model of the central part of the 20-atom h-BN-20 model; **c)** similar model of the h-BN layer from [62]

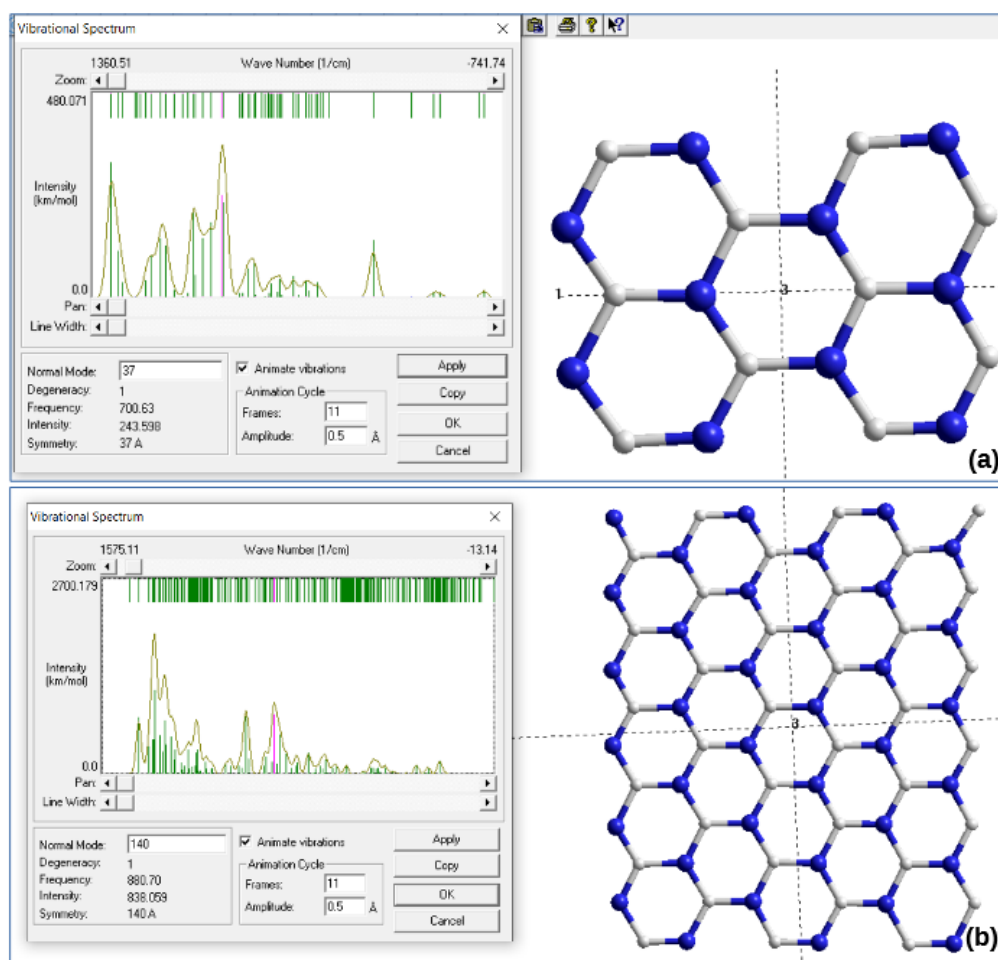


Fig. 10. Examples of calculated vibrational spectra: **a)** for the model h-BN-20, **b)** for the model h-BN-72

Calculations of vibrational modes for these models in the HyperChem program allowed us to obtain the fundamental vibrational spectra of lamellar boron nitride layers. Examples of the calculated vibrational spectra are shown in Figure 10. The fundamental modes are listed in Table 3. The obtained vibrational mode data are consistent with known data for layered structures of the h-BN [64].

Analysis of the obtained vibrational mode spectra of boron nitride layers, compared with literature data [64], revealed that the fundamental vibrational modes are clearly distinguished, are quite stable, and lie in three main ranges.

In the vibrational spectrum, these ranges can be distinguished as three sets of IR-active phonon bands. The first set, A, is in the range of $0\text{--}600\text{ cm}^{-1}$ (from $16.7\text{ }\mu\text{m}$ and onward), and the corresponding frequencies regularly tend to zero with increasing n . As shown in the paper [64], these normal modes are associated with the elastic and piezoelectric tensors of the h-BN monolayer. The second set, B ($600\text{--}800\text{ cm}^{-1}$, corresponding to the range from 16.7 to $12.5\text{ }\mu\text{m}$), and the third, C ($1300\text{--}1600\text{ cm}^{-1}$, corresponding to the range from 7.7 to $6\text{ }\mu\text{m}$), regularly tend to the optical modes of the h-BN layer and correspond to the LWIR range.

Thus, these ranges (especially the later long wavelengths) precisely correspond to the required characteristics for far-infrared detectors [26–30].

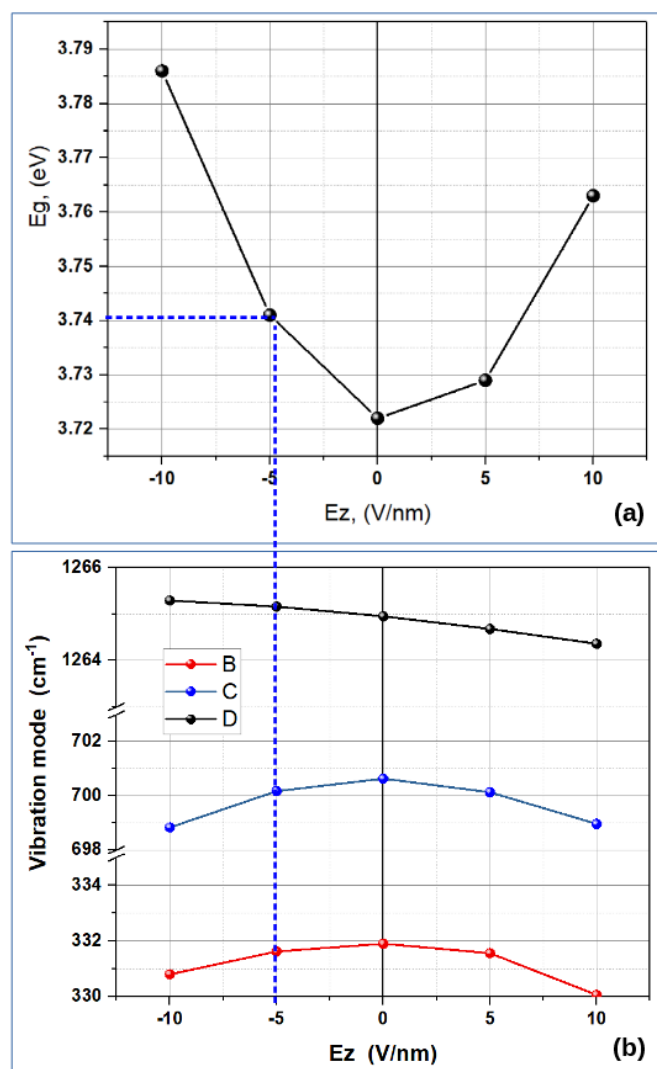


Fig. 11. Dependence of the energy band gap E_g and the main vibration modes from the applied electric field E_z for h-BN-20 model.

In this study, we then calculated the electronic energy characteristics and vibrational mode spectra as functions of the applied external electric field voltage on models in the direction perpendicular to the h-BN layer, i.e., with variations in the E_z component of the electric field. The resulting calculated data are presented in Figure 11 and Table 4. A clear dependence on the electric field intensity E_z is evident here: shifts of all electronic levels and the band gap E_g occur, and the fundamental vibrational modes smoothly change.

Table 4. Dependence of the electron energy levels for h-BN-20 model from the electric field E_z in PM3 RHF

E_z , V/nm	E_{HOMO} , eV	E_{LUMO} , eV	E_g , eV	D_z , Debye	D_t , Debye	ν_1 , cm^{-1}	ν_2 , cm^{-1}	ν_3 , cm^{-1}
-10	-7.978	-4.192	3.786	2.873	5.2737	330.8	698.83	1265.29
-5	-7.958	-4.217	3.741	1.423	4.697	331.62	700.17	1265.16
0	-7.951	-4.228	3.722	-0.035	4.497	331.9	700.63	1264.95
5	-7.956	-4.227	3.729	-1.488	4.723	330.56	700.13	1264.68
10	-7.974	-4.211	3.763	-2.937	5.319	330.93	698.69	1264.36
h-BN +PVDF	-7.457	-3.716	3.741			332.06	699.96	1264.35

As noted above, ferroelectric PVDF and PVDF-TrFE layers are used to generate the control electric field in various heterostructures for photo and infrared radiation sensors [26–30].

In this case, a similar PVDF model (Fig. 6.) and calculation of the electric field using formulas (1) and (2) yields the following electric field (taking into account the permittivity for h-BN, which is equal to $\varepsilon = \sim 2-4$ [65]): for $\varepsilon = 2$ the value of $E_z^* = \sim 5$ V/nm; and if $\varepsilon = 3$ the $E_z^* = \sim 3.3$ V/nm.

These electric field values here fit well within the range (rank) of the electric field values used in the calculations and are quite suitable values.

Note that the electric field created by the polarization of such a ferroelectric layer also affects the characteristics of the h-BN layers, just like the applied external field, and thus changes and regulates their properties. To simulate this effect, we considered a model of the PVDF + h-BN heterostructure in different variants of the h-BN layer model (Fig. 12).

For our estimation of the h-BN and PVDF models (Fig. 6 and Fig. 12) in this work and the data presented in Table 4 for the data for the $E_g(E_z)$ dependence for h-BN, we can see that $E_g = \sim 3.74$ eV for $E_z = -5$ V/nm, while for $E_z = 0$ value of $E_g = 3.722$ eV (computed by PM3 RHF method). Thus, this value of the electric field causes a shift in E_g .

Comparing these data with the results of the calculations of the model h-BN+PVDF for h-BN-20 model (see Fig. 12a), presented in the last bottom row of Table 4, we see that the value of $E_g = \sim 3.74$ eV in the h-BN structure occurs precisely under the influence of the electric field created by the polarization of the PVDF chain $E_z \sim |5|$ V/nm. Thus, we obtained data $E_z^* \sim 5$ V/nm for PM3 RHF calculations.

Furthermore, examining the change in the fundamental vibrational frequencies of the h-BN layer under the influence of an applied electric field (Table 4, the last three columns, and Fig. 11), we see that this field also alters the vibrational mode values.

Thus, it is shown here that the electric field from the polarization of the ferroelectric layer influences and modifies the fundamental frequencies or vibrational modes in the far-infrared range of interest to us. Thus, it is clear that such an h-BN+PVDF heterostructure can form the basis of an adjustable sensor in the far-infrared range.

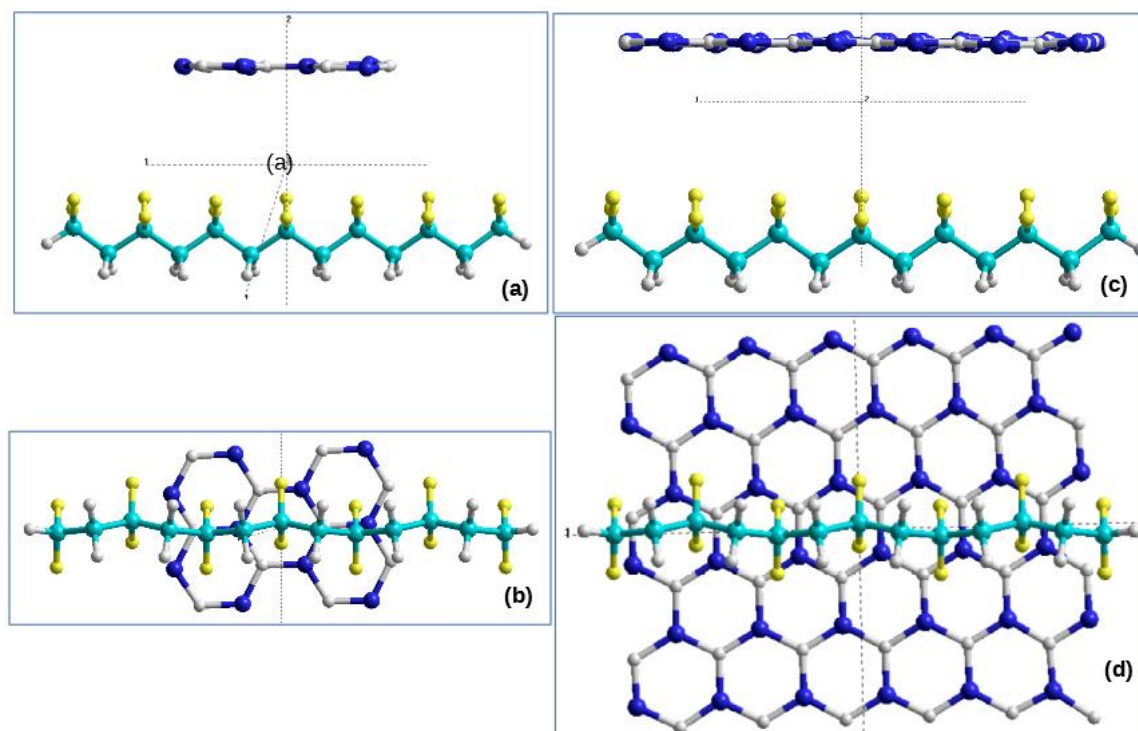


Fig. 12. Model of interacting PVDF and h-BN layers: **a)** and **b)** side along Y-axis and top along Z-axis view for h-BN-20 model, **c)** and **d)** side along Y-axis and top along Z-axis view for h-BN-72 model

3.3 Modelling and computational data for Graphene structure

Graphene is a two-dimensional structure of carbon atoms [2, 4]. A clear and simple description of the graphene single-layer structure and its electronic bonds is presented in book [66]. A carbon atom has six electrons occupying the $1s^2$, $2s^2$, $2p_x$, and $2p_y$ atomic orbitals [66]. When carbon atoms are brought together, one electron from the $2s$ orbital is promoted to the $2p_z$ orbital for the formation of hybrid orbitals. In diamonds, the $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals are mixed to form four sp^3 hybrid orbitals for each carbon atom; therefore, each carbon atom is joined with four neighbors by overlapping their sp^3 hybrid orbitals. In graphite, instead of four sp^3 hybrid orbitals, three sp^2 hybrid orbitals are formed through mixing of the $2s$, $2p_x$, and $2p_y$ orbitals, while the fourth orbital remains as $2p_z$. Overlapping sp^2 hybrid orbitals from two adjacent atoms creates a strong σ covalent bond (C-C bond); these in-plane σ bonds connect each carbon atom to three neighbors. The remaining $2p_z$ orbitals of these carbon atoms form π bonds, which are responsible for binding carbon layers together in graphite. Because π bonds are much weaker than σ bonds, graphite has a low shear strength so that its carbon layers can be easily detached. For monolayer graphene, these nearly free π electrons are responsible for most of its experimentally observed electronic and optical properties. Because the Pauli Exclusion Principle requires that π electrons from different carbon atoms do not occupy the same state, the large number of closely packed carbon atoms in graphene causes degenerate energy levels to split into continuously distributed nondegenerate levels of allowed energy states, forming energy bands. The real-space two-dimensional honeycomb lattice of graphene is shown in Figure 13a. The distance between two neighboring carbon atoms in graphene is $a = 1.42 \text{ \AA}$ [66].

The honeycomb lattice of graphene is not a Bravais lattice because the locations of all carbon atoms cannot be generated by the translation $\mathbf{R} = m \cdot \mathbf{a}_1 + n \cdot \mathbf{a}_2$, where m and n are integers. The lattice structure of graphene consists of two overlapping Bravais sublattices A and B, and thus a primitive unit cell contains two carbon atoms, as shown in Figure 13a. All of the carbon atoms on the same sublattice, but not those on two different sublattices, are connected by the vector $\mathbf{R}$.

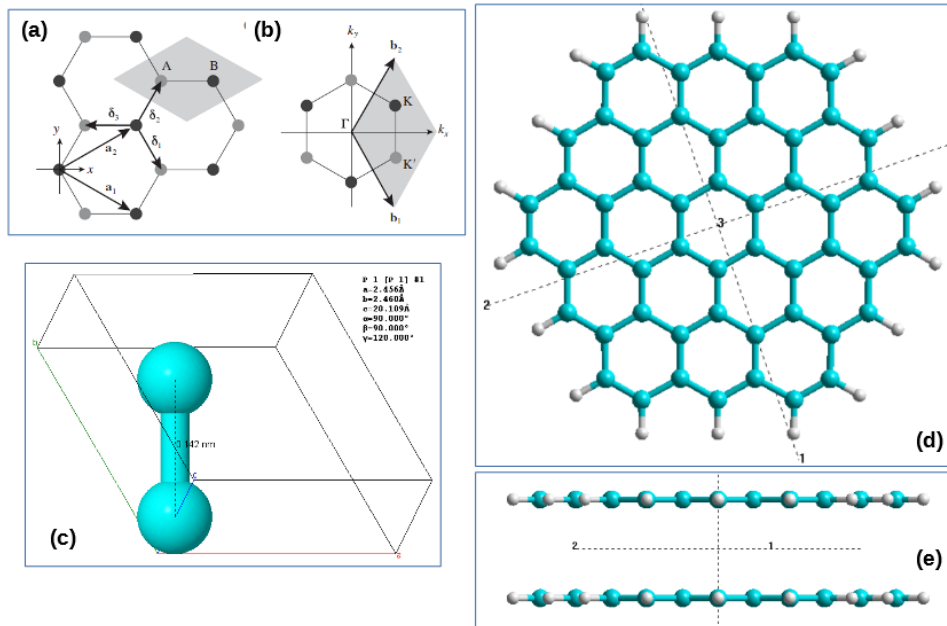


Fig. 13. (a) Real-space graphene lattice. The lattice consists of two overlapping Bravais sublattices, A (gray dots) and B (black dots). The primitive unit cell is drawn as a shaded area. Vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are the primitive lattice vectors; δ_1 , δ_2 , and δ_3 are vectors pointing from a B atom to its nearest A atoms. (b) Brillouin zone of graphene drawn as a shaded area. Vectors $\mathbf{b}_1$ and $\mathbf{b}_2$ are the primitive vectors of the reciprocal lattice. Dirac points K (black dots) and K' (gray dots) are marked (these images presented from book [66]). (c) View of unit cell in Jmol after Quantum ESPRESSO [48] calculation. (d) and (e) Graphene one-layer and two-layers models with 54 C atoms arranged by Hydrogen atoms (model Gr54H) from our works [31, 36] build in the HyperChem work space [51]

The energy band structure of graphene has its own characteristic features, which have been examined and studied in detail in a number of studies [1–4]. Here we briefly describe the main features of the graphene band structure following [66].

The electronic band structure of graphene can be obtained by using the tight-binding model, usually described using a tight-binding Hamiltonian $\mathbf{H}$ for the Schrödinger equation. The solution to this equation is the wave function, which is given by a linear superposition of the orbital functions. However, a difficulty in obtaining a solution arises here, since the atoms on sublattice A are not geometrically identical to the atoms on sublattice B. To avoid this difficulty, the solution is simplified by adopting an approximate approach that takes into account only the self-interaction of each carbon atom at a lattice point and the interactions of the atom with its three nearest neighbors; all long-range interactions are assumed much weaker than these interactions and are thus ignored.

As a result, after a series of transformations, the energy eigenvalues can be written as

$$E(\mathbf{k}) = \varepsilon \pm 3\gamma_0 \cdot f(\mathbf{k}) \quad (3)$$

where ε is the self-interaction energy, and γ_0 is the nearest-neighbor hopping energy in graphene. The nearest-neighbor hopping energy γ_0 is experimentally measured to have a value of $\gamma_0 = 3.16$ eV [2–4], which is the same as that found for graphite.

At the Γ point ($\mathbf{k} = 0$), we find the eigenenergies $E = \varepsilon \pm 3\gamma_0$ from (3), which are associated with the eigenstates of the solutions for sublattices A and B, respectively. The eigenenergy $E = \varepsilon - 3\gamma_0$ for the valence band is associated with symmetric bonding orbitals such that the amplitudes of the wave functions for sublattices A and B have the same sign. By contrast, the eigenenergy $E = \varepsilon + 3\gamma_0$ for the conduction band is associated with antibonding orbitals such that the amplitudes of the wave functions for sublattices A and B have opposite signs.

The conduction band (π^* band) and the valence band (π band) are symmetric with respect to the $E = 0$ plane, as shown in Figure 14a. Note that the long-range interactions of carbon atoms beyond the nearest neighbors are usually ignored for simplicity. When these long-range interactions are accounted for, we find that the π^* and π bands are actually not symmetric to each other, as seen in Figure 15b below, where we also show the σ^* and σ bands contributed by the σ bonds.

As can be seen in Figure 14a, the conduction band touches the valence band at $E = \varepsilon$. The self-interaction energy ε can be taken as the reference level by setting it to be 0 for simplicity so that an electron in a state on the conduction band has a positive energy and that in a state on the valence band has a negative energy. Then, (3) can be simplified as

$$E(\mathbf{k}) = \pm 3\gamma_0 \cdot f(\mathbf{k}), \quad (4)$$

where the plus sign represents the conduction band and the minus sign represents the valence band. The points at $E(\mathbf{k}) = 0$ are called the Dirac points; the vicinities of these points are referred to as the valleys, where the graphene band structure can be described by the relativistic Dirac equation, which is discussed in the book [66].

Corresponding to the two distinct sublattices A and B in the real space, there are two distinct groups of Dirac points $\mathbf{K}$ and $\mathbf{K}'$ in the k -space. Inside the Brillouin zone drawn in Figure 14b, two Dirac points can be found at the k -space locations represented by the reciprocal space vectors: $\mathbf{K}$ and $\mathbf{K}'$ (see Fig. 13a).

Another popular choice of the k -space locations of $\mathbf{K}$ and $\mathbf{K}'$ in the literature is to select the $\mathbf{K}$ and $\mathbf{K}'$ points on the k_y axis so that they are mirror symmetric with respect to the k_x axis; the physics and the results obtained in the following remain unchanged when using this alternative selection. It can be easily shown using (4) that $E(\mathbf{K}) = E(\mathbf{K}') = 0$ at these Dirac points.

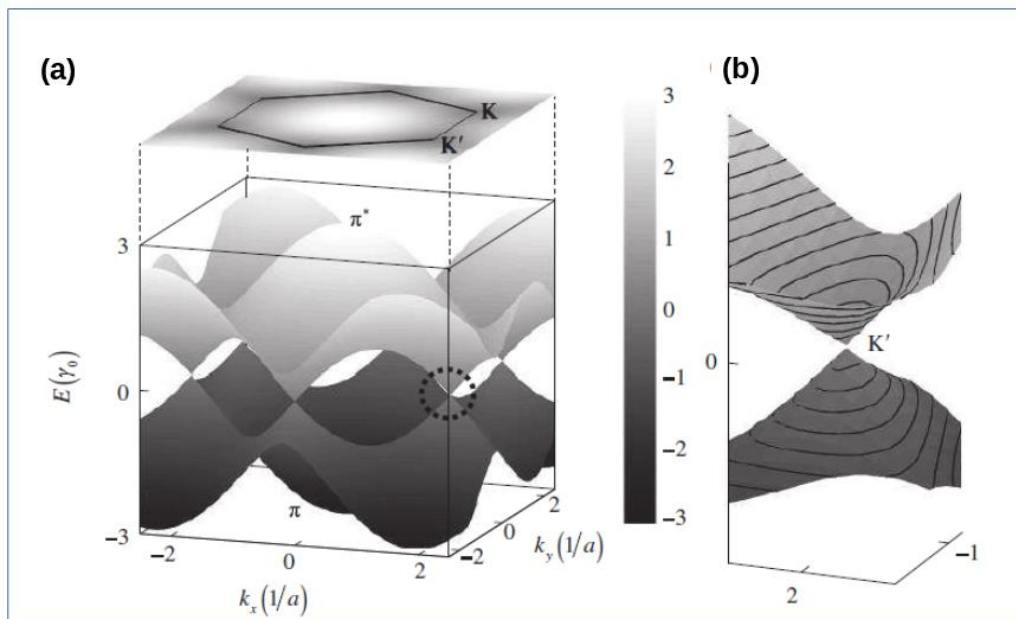


Fig. 14. (a) Band structure of graphene plotted using (3) while setting the self-interaction energy to be $\varepsilon = 0$ [66]. The top surface of a higher energy is the conduction band (π^* band), and the bottom surface of a lower energy is the valence band (π band). The conduction band is projected onto a two-dimensional plane on the top. The circled region near the Dirac point $\mathbf{K}'$ is enlarged in (b) (from [66])

Our *ab initio* modeling of graphene was performed using density functional theory (DFT) methods using the Quantum ESPRESSO software package [48], and quantum chemical calculations were performed using semi empirical PM3 methods [42–44] in the restricted Hartree-Fock (RHF) approximation in the HyperChem program [51]. For the DFT calculations, the Perdew-Burke-Ernzerhof (PBE) parameterization and the generalized

gradient approximation (GGA) [47] were used. The following simulation parameters were used: the wave function cutoff energy was 50 Ry ($1 \text{ Ry} \approx 13.605 \text{ eV}$), the charge density and potential cutoff energy was 700 Ry, and the Brillouin zone was represented using a $12 \times 12 \times 1$ Monkhorst-Pack grid. To eliminate possible parasitic energy oscillations during the simulation, a 20 Å thick vacuum layer (along *c*-axis) was added to the structure under study. Initially, iterative procedures were performed using the Quantum ESPRESSO software package to determine the unit cell parameters used to describe the structure under study. The primary unit cell parameter chosen for graphene was $a = 2.456 \text{ Å}$.

The results of the obtained DFT calculations are presented in Figure 15. As can be seen, the main branches of the calculated energy band structure diagram are in good agreement with other known data [1–4, 66]. In particular, the Dirac cone also appears at point K. The energy values (energy gaps) at point G are $E_g(\text{G}) = 6.2927 \text{ eV}$, and at point M is equal $E_g(\text{M}) = 3.9847 \text{ eV}$. This is also consistent with the data [1–4, 66].

Next, as above, we are interested and focused in the dependence of the main energy gap E_g on the electric field E . We also need to determine the core vibrational modes of the graphene and their dependence on the applied electric field E and compare them with the influence of the electric field from the used ferroelectric PVDF layer. For all these calculations, we used the Gr54H model (consisting of a layer of 54 carbon atoms C arranged with hydrogen atoms H to stabilize the system), which we developed previously and used in our work [31, 32, 35, 36] (Fig. 13d, e).

It should be noted here that the vibrational modes of graphene have already been studied quite well and are known [67]. In particular, graphene has a G-peak ($\sim 1580 \text{ cm}^{-1}$) – this is the fundamental scattering mode. Figure 16 shows experimental data on the Raman spectra from [68]. We further perform all these calculations also using the HyperChem program [51]. The computed data on the electron energy and series of the vibration modes are presented in Table 5.

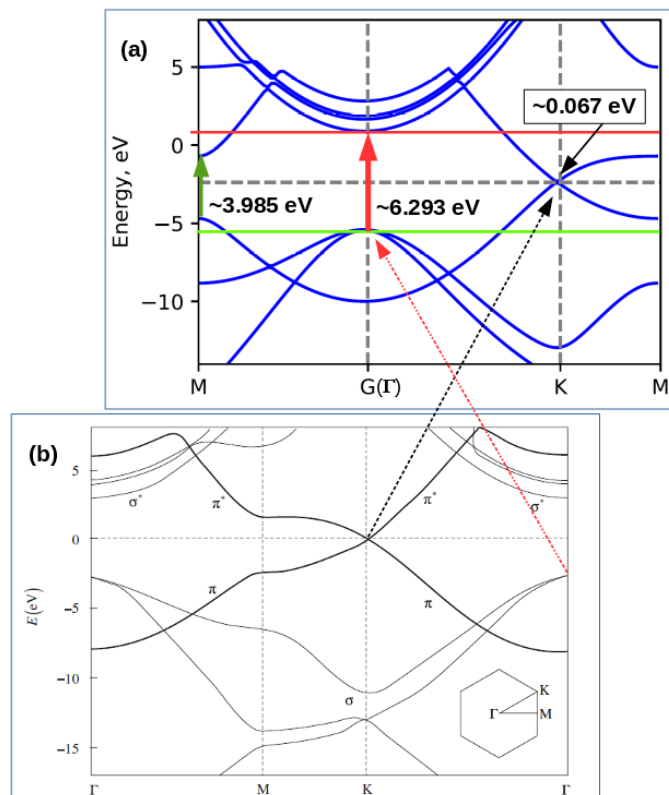


Fig. 15. G3. The energy band structure of Graphene calculated using the Quantum ESPRESSO program (a), compared with data (b) full band structure of graphene from [66] (the thick curves are the π^* and π bands, and the thin curves are the σ^* and σ bands)

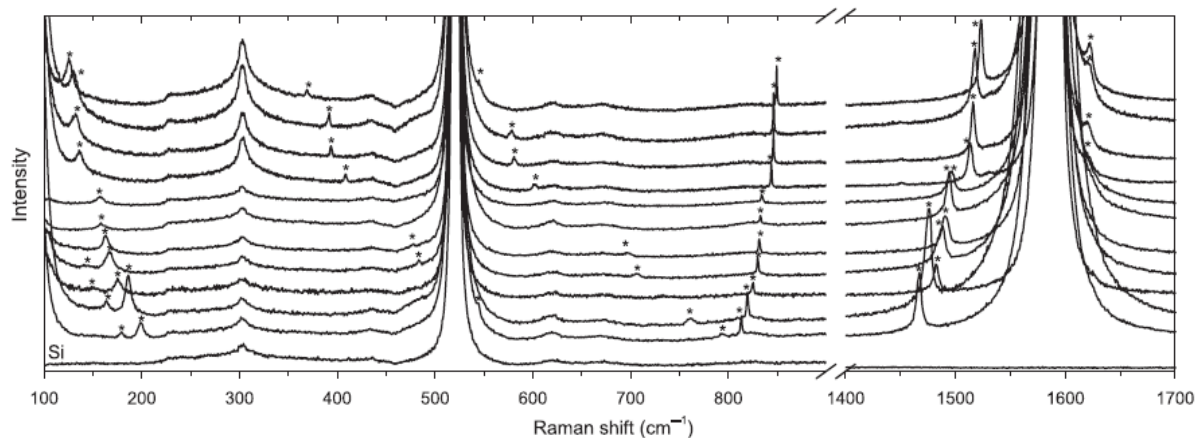


Fig 16. Experimental Raman spectra from twisted bilayer graphene (tBLG) [68]. The peaks marked with * are activated by the superstructure modulation. The peaks at 303 cm^{-1} and 512 cm^{-1} come from the Si substrate where the sample is sitting. The peak at 1584 cm^{-1} is the G band.

Table 5. Dependence of the electron energy levels for Graphene (model Gr54H) and key vibration modes from the electric field E_z , computed using PM3 RHF method (HyperChem)

E_z , V/nm	E_{HOMO} , eV	E_{LUMO} , eV	E_g , eV	D_z , Debye	D_b , Debye	ν_0 , cm^{-1}	ν_1 , cm^{-1}	ν_2 , cm^{-1}	ν_3 , cm^{-1}	ν_4 , cm^{-1}	ν_5 , cm^{-1}	ν_6 , cm^{-1}
-20	7.6192	-1.8804	5.7389	7.169	7.169	204.09	248.68	537.13	734.12	913.10	1422.9	1573.1
-15	-7.6179	-1.8687	5.7492	5.375	5.375	212.76	250.93	550.03	744.52	947.86	1423.5	1573.4
-10	-7.6168	-1.8601	5.7567	3.581	3.581	218.71	251.04	555.14	757.50	969.61	1423.9	1573.6
-5	-7.6161	-1.8550	5.7612	1.789	1.789		222.19	555.55	758.18	969.64	1424.1	1573.7
0	-7.6259	-1.8532	5.7838	-0.002	0.003	223.36	250– 300	500– 565	758– 760	960– 970	1380– 1470	1570–1650
5	-7.6161	-1.8548	5.7612	-1.794	1.794		251.7	555.54	758.18	969.64	1424.1	1573.7
10	-7.6166	-1.8599	5.7567	-3.586	3.586		251.04	555.14	757.68	969.60	1423.9	1573.6
15	-7.6176	-1.8683	5.7493	-5.379	5.378		250.93	550.04	744.51	947.80	1423.5	1573.4
20	-7.6190	-1.8801	5.7389	-7.173	7.173		250.78	529.38	734.11	912.9	1423.0	1573.11
From [68]							303	512	820–850	~ 1470– 1500		1584
Gr54H + PVDF	-7.2106	-1.4604	5.7838	13.87	13.89		215.42 281.84	506.08 598.91	758.40 767.96	953.32 959.91	1324.5 1498.2	1553.8 1573.9
Gr54H + PVDF rot180	-8.0797	-2.3440	5.7357	-14.3	14.35		214 281	506 598	758.26 766.41	955.54 969.65	1323.9 1497.6	1554.01573.5

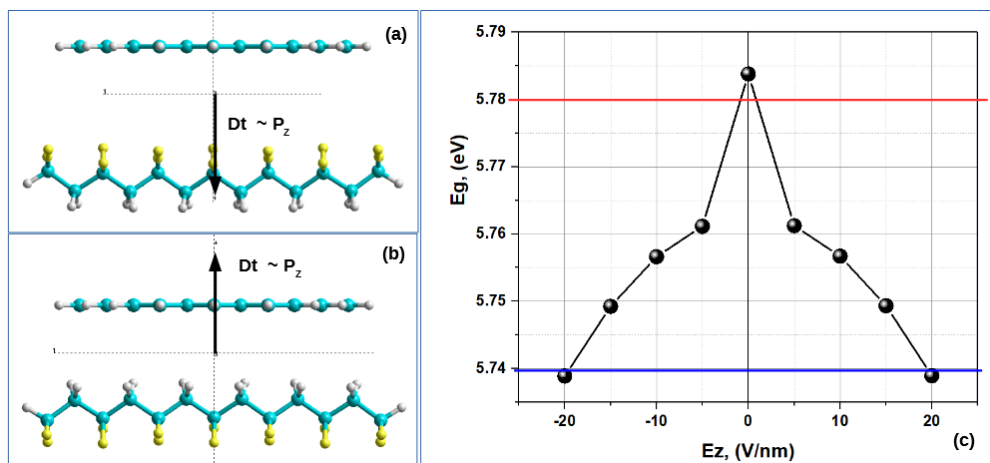


Fig. 17. Dependence of the energy band gap E_g from the applied electric field E_z for graphene one layer model: **a)** and **b)** show oppositely directed dipole moments and polarization for different PVDF orientations; **c)** the marked line (red and blue) show the E_z field created by PVDF of different orientations, corresponding to the various E_g values levels

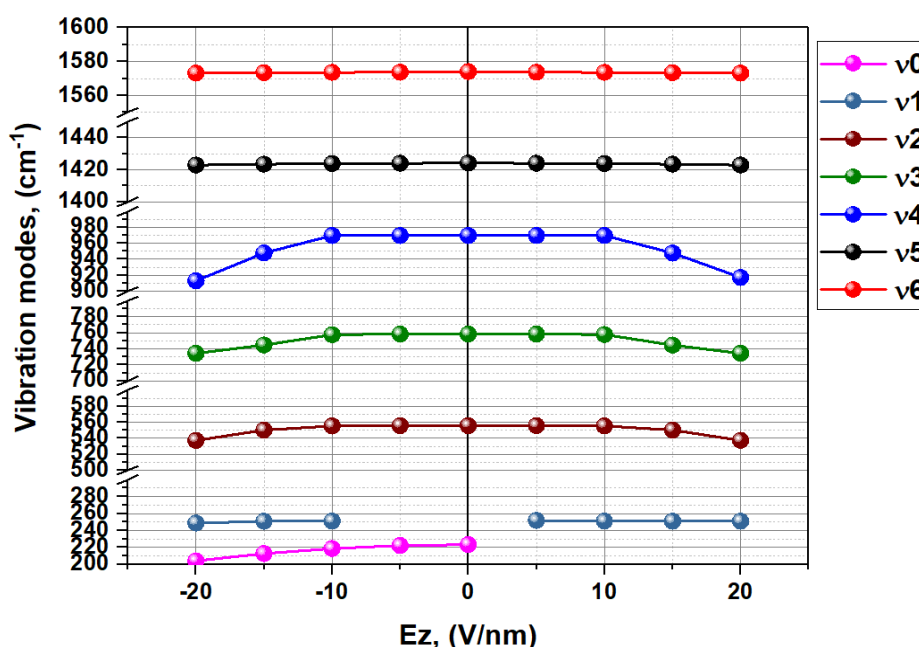


Fig. 18. Dependence of the main vibration modes from the applied electric field E_z for graphene one layer model

Calculations of vibrational modes for these models using the HyperChem program allowed us to obtain the fundamental vibrational spectra of one layer Graphene Gr54H model. Examples of the calculated vibrational spectra are shown in Figure 19.

In summary, the data obtained from modelling and performing all these calculations on the change in the band gap E_g and vibrational modes in single-layer graphene (Gr54H model) depending on the applied electric field E clearly demonstrate the existence of such dependencies (see in Table 5 and Fig. 17, Fig. 18).

Thus, these obtained dependences for graphene also indicate the possibility of controlling the electronic and vibrational properties of the graphene layer from the ferroelectric layer due to its electric field generated by the polarization within it.

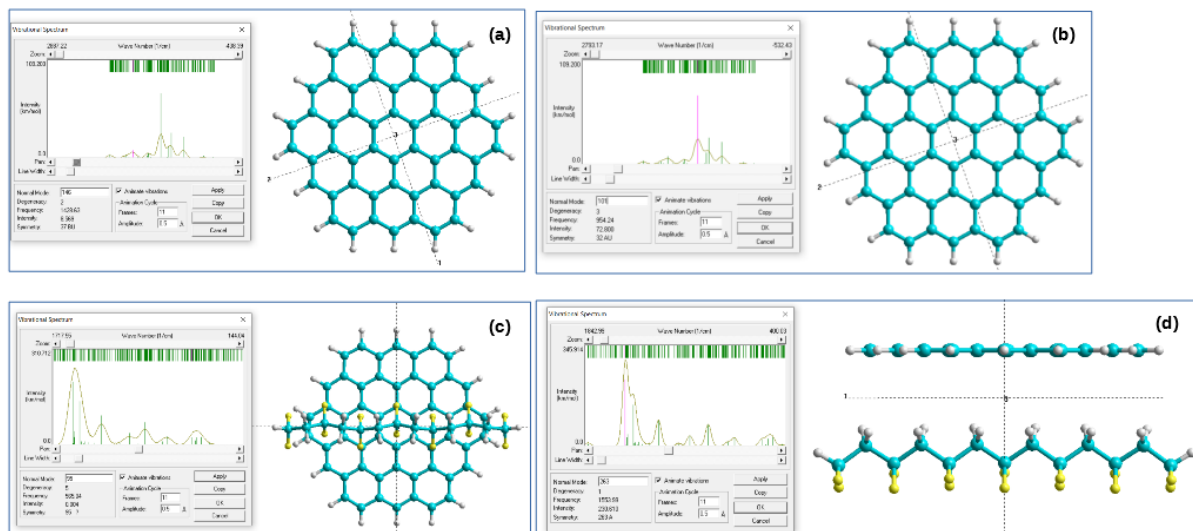


Fig. 19. Examples of calculated vibrational spectrum for graphene: **a)** and **b)** for Gr54H model in Z-plane view; **c)** and **d)** for the model Gr54H+PVDF in Z-plane and along Y-axis

The modeling of two-dimensional nanostructures (based on dichalcogenides of the transition metals – TMD such as MoTe₂, boron nitride H-BN and graphene layers) combined in a heterostructure with a layer of ferroelectric polymer PVDF, as well as calculations using DFT and semiempirical quantum chemical methods, showed that both the band gap of these nanomaterials and their vibrational modes (especially important in the infrared range) clearly depend on the applied electric field intensity E . This includes the electric field generated by the ferroelectric layer due to its inherent internal polarization. This means that these two-dimensional nanostructures and heterostructures, combined with a ferroelectric layers, can be used as elements for creating controlled and adjustable electromagnetic radiation sensors and wide-range detectors. This is especially important in the infrared and far-infrared ranges.

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