

Vibrational properties of hybrid halide perovskite for solar cells applications

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Abstract

Les propriétés électroniques remarquables de l'iodure de méthylammonium de plomb rendent ce matériau prometteur pour une large gamme d'applications, notamment dans le domaine du photovoltaïque. Le $\text{CH}_3\text{NH}_3\text{PbI}_3$ ainsi que d'autres matériaux hybrides en structure perovskite présentent tous un gap d'énergie allant de 1.1 à 2.1 eV dans la région visible du spectre, favorable aux applications photovoltaïques. Cette classe de matériaux possède également un grand coefficient d'absorption, de faibles masses effectives pour les porteurs de charge et de grandes mobilités de ces porteurs.

L'objectif de ce travail est de comprendre les propriétés vibratoires à basse température de ce matériau et d'en extraire le lien avec les propriétés de transport. Les propriétés structurales, électroniques, vibratoires et diélectriques de ce matériau sont déterminées théoriquement par calcul *ab initio* basé sur la théorie de la fonctionnelle de la densité perturbée et sont comparées tant que possible avec des résultats expérimentaux extraits de la littérature.

Plusieurs propriétés du $\text{CH}_3\text{NH}_3\text{PbI}_3$ sont évaluées, comprenant les paramètres de maille de la structure relaxée, le band gap électronique, les charges effectives de Born, les tenseurs diélectriques et les intensités infrarouges. La correspondance avec les résultats expérimentaux varie en fonction de la propriété étudiée, allant d'acceptable à excellente.

Différents cas seront distingués en fonction de la prise en compte ou non de plusieurs phénomènes physico-chimiques intervenant dans un tel matériau. Parmi ceux-ci, le couplage spin-orbite et les interactions de van der Waals dont le rôle est encore peu implémenté d'un point de vue théorique.

Cette étude confirme l'importance de la prise en compte de ces effets afin d'obtenir une représentation plus réaliste des propriétés du matériau.

Abstract

The outstanding electronic properties of methylammonium lead iodide make it attractive for a wide range of applications, particularly in the photovoltaic field. $\text{CH}_3\text{NH}_3\text{PbI}_3$ as well as other closely related hybrid perovskites all display band gaps from 1.1 to 2.1 eV in the visible light range, favorable for photovoltaic applications. This class of materials also exhibits a large absorption coefficient, low dual electron and hole effective masses and high carrier mobilities.

The aim of this work is the understanding of the vibrational properties of the stable phase of the material at low-temperature and the extraction of the link with the outstanding transport properties. The structural, electronic, vibrational and dielectric properties of this material are theoretically determined by an *ab initio* calculation based on the Density Functional Perturbation Theory and are compared as much as possible with experimental results found in the literature.

Several properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ are characterized, including the lattice parameters of the relaxed structure, the electronic band gap, the Born effective charges, the dielectric tensors and the infrared intensities. The agreement with the experimental results varies depending on the studied property.

Different cases will be distinguished according to the inclusion or not of several physico-chemical phenomena involved in such a material. Among them, the spin-orbit coupling and the van der Waals interactions whose role is still not enough implemented from a theoretical point of view.

This study confirms the importance of taking these corrections into account in order to get more realistic material properties.

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Introduction

Solar cells are usually divided into three categories called generations according to their production cost (in $\text{\$/cm}^2$) and efficiency, which both determine the price of solar energy in $\text{\$/kWh}$. The 1st generation (crystalline silicon) shows high-cost and moderate efficiencies ($\sim 20\%$). The 2nd generation (highly absorbing thin film materials) brings the solar energy price down by lowering the material's cost while keeping high enough efficiencies. Finally, the 3rd generation is expected to combine low cost and high efficiency but it is only purely conceptual at this stage. Nowadays, the 1st generation, silicon-based technology, occupies by far the largest market share. Lowering significantly the price of solar energy requires the large deployment of 2nd generation devices.

In this framework, hybrid organic-inorganic perovskite cells have attracted considerable attention. Indeed, the complex integration of organic and inorganic components allows the combination of interesting properties from both components in a unique material. Inorganic compounds provide a wide range of electronic properties such as a high electron mobility, a wide range of band gaps, thermal stability and mechanical hardness, while organic compounds offer the potential of high luminescence efficiency and plastic mechanical properties. As a result, the power conversion efficiency of these perovskite cells has increased from 3.8% reported by Miyasaka et al. in 2009 [15] to the current record of 22.1% [1, 13, 16] (figure 1), by optimizing the crystalline quality of the perovskite absorber and the film formation by solvent engineering. It was obtained for the particular hybrid halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ which has become a prominent material for solar cells applications.

This family of materials exhibits a lot of properties ideal for photovoltaics such as high dual electron and hole mobility, large absorption coefficients, a favorable gap, an adjustable spectral absorption range, long diffusion lengths, a strong defect tolerance and the affordability of fabrication [16]. A unique property of these materials is the ability to both act as light-harvesting medium and as charge carrier transporter. As the underlying reasons of this success are not yet fully understood, it could be interesting to gain a better understanding of these materials.

The hybrid halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ exhibits a complex structural behavior with several phase transitions between orthorhombic $Pnma$ (below 162.2 K), tetragonal $I4/mcm$ (between 162.2 and 327.4 K), and cubic $Pm\bar{3}m$ (above 327.4 K) polymorphs. In the ABX_3 perovskite structure, the A cation is at the center of a cube formed of corner-sharing BX_6 octahedra [13].

My master thesis is mainly focused on the simulation of the vibrational properties of methylammonium lead iodide allowing the understanding of its outstanding performance. The structural, electronic and vibrational properties are numerically calculated thanks to *ab initio* simulations using Density Functional Perturbation Theory (DFPT) as implemented by ABINIT [17, 18]. Simulations are performed for the low-temperature phase because the configuration of the CH_3NH_3^+ cations is well-defined in the orthorhombic phase, while the angular disorder increases with the temperature. Moreover, at low temperature the molecules are constrained in the orthorhombic phase and harmonically vibrate around their equilibrium

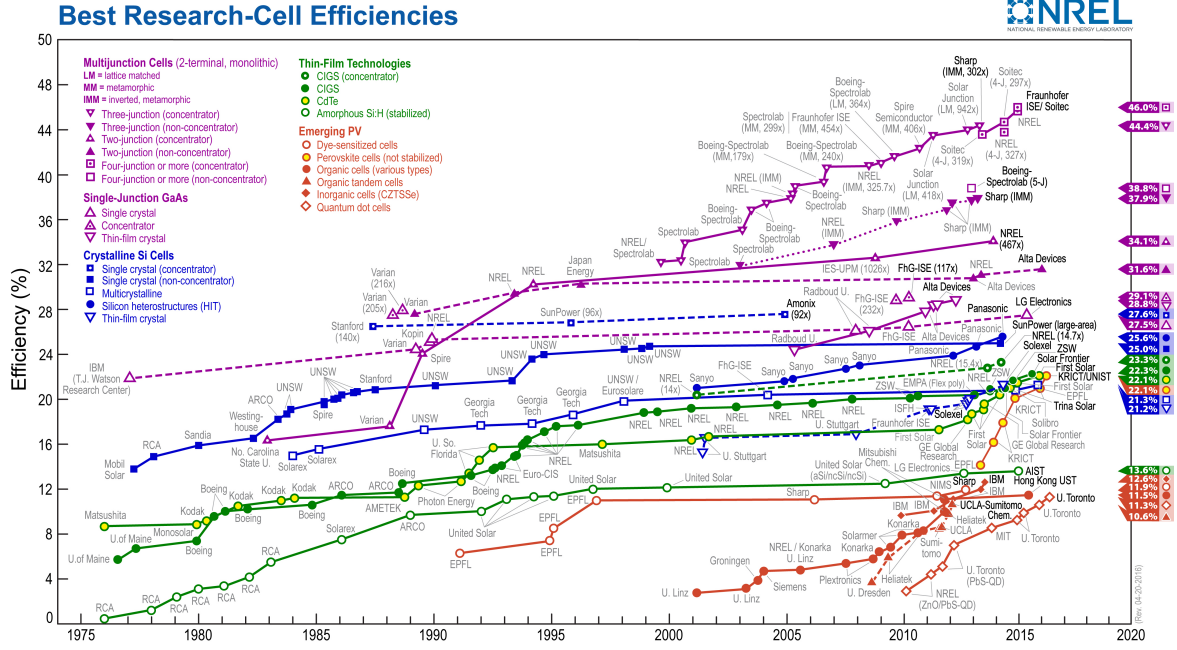


Figure 1: Best research-cell efficiencies reported by the National Renewable Energy Laboratory (NREL) [1]. The record for perovskite cells of 22.1% has been established by the Korea Research Institute of Chemical Technology (KRICT) and the Ulsan National Institute of Science and Tehcnology (UNIST).

position, while a temperature increase gives rise to a complex anharmonic dynamics with fast reorientations [19]. The harmonic approximation is therefore used in our calculations. Results for the low-temperature (orthorhombic) phase are crucial to understand the properties observed in the room-temperature (tetragonal) phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$. The spin-orbit coupling and the van der Waals corrections are also included and modeled in order to get a better interpretation and comparison with experimental results mentioned in the literature.

The manuscript is organized as follows: In section 1, a quick overview of the materials that are currently used in solar cells or that are in the heart of the research is established. The outstanding properties of hybrid perovskite materials are discussed as well as their strengths and weaknesses. In section 2, the crystallographic structure of perovskite materials, and more particularly of $\text{CH}_3\text{NH}_3\text{PbI}_3$, is studied and the several phase transitions are discussed. Additionally, some synthesis routes for hybrid perovskite materials are presented. Theoretical concepts on numerical simulations performed in this work are detailed in section 3 and starts from the multi-body problem to the Density Functional Theory (DFT) and Density Functional Perturbation Theory (DFPT). Moreover, van der Waals dispersive corrections and relativistic spin-orbit effects are discussed from a theoretical point of view. Section 4 discusses the results of calculations, focusing on one hand on the electronic properties (section 4.1) and on the other hand on the vibrational properties (section 4.2). The 144 normal modes of vibration are determined and a factor group analysis is used to characterize the infrared and Raman activities of each mode. In addition, different properties are studied such as the Born effective charges, the optical and static dielectric constants, and the LO-TO splitting. For completeness, we also analyze the sensitivity of the electronic and vibrational properties to the inclusion of van der Waals interactions and relativistic effects. Finally, in section 5, our results are discussed and compared with results from other works. A comparison between theory and experiment is also mentioned. In section 6, we summarize our findings and offer our conclusions.

Chapter 1

State-of-the-art of hybrid halide solar cells

In 90 minutes, enough sunlight strikes the earth to provide enough energy needed for one year for the entire planet. The main aim of research consists in finding a way to efficiently capture this energy and use it. The transformation of solar energy has reached its most critical point when solar cells were designed. The cells use the solar energy to convert the light to photon generated voltages, commonly known as photovoltaic. A typical photovoltaic cell usually absorbs only the visible part of the solar radiation, corresponding to 46% of the total solar radiation. The other 54% of solar energy correspond to infrared and ultraviolet radiations and are either absorbed by the earth surface or reflected back to the space. The conversion of energy of light into electricity involves 3 basic steps. Firstly, the absorption of sunlight followed by the generation of electron-hole pairs or excitons. Indeed, once excited, an electron can be promoted from the ground-state to the excited state. Such excited electron can either dissipate energy as heat by recovering its initial orbital or travel through the cell. Secondly, charge carriers of opposite types, namely electrons and holes, are separated. Eventually, charge carriers are extracted to an external circuit.

Solar cell technologies are traditionally divided into three generations.

The first generation includes panels made of crystalline silicon wafers that typically demonstrate an efficiency of 25%. Silicon is a market-leading photovoltaic technology due to its good performance, as well as its high stability. Silicon panels can last for 30-plus years without showing any deficiency. However, silicon's record efficiency has only increased from 25.0% to 25.6% in the previous 15 years [20]. Moreover, they are rigid and require a lot of energy for their production.

The second generation solar cells are thin film solar cells and include amorphous silicon, CIGS and CdTe cells. These second generation solar cells require less energy for their production and have a lower material consumption, allowing to reduce the production cost [21]. However, the second generation solar cells are based on scarce elements which limits the cost reduction.

The third generation solar cells are mainly based on organic materials. They also include a lot of thin film technologies using organic materials, or organometallic compounds as well as inorganic substances. A new class of thin film solar cells currently under investigation are perovskite solar cells, typically solution-processed hybrid organic-inorganic tin or lead halide based materials. Compared to silicon, perovskites offer a remarkable processing flexibility and quick and inexpensive large-scale production. The efficiency of perovskite solar cells has quickly increased during the last decade, reaching the current record of 22.1% [1]. Regardless of application, stability has been a critical issue for perovskites as they can degrade easily in humidity. Despite this low stability and the lower efficiency compared to first and second

generation solar cells, perovskites have great potential thanks to their low-cost production, making them very attractive for commercialization.

Hybrid organic-inorganic perovskites (HOIPs) are well-known for many years. A global timeline shown in figure 1.1 synthesizes the most important steps about the perovskite synthesis since its discovery. Weber was the first who synthesized $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) and determined its crystal structure in 1978 [22]. During the 1990s, several researches have been led on the synthesis and the characterization of HOIPs. Among them, Mitzi and coworkers at International Business Machines (IBM) Yorktown laboratories focused on the use of HOIPs in electronic devices [23–27]. The first incorporation into solar cell was reported by Miyasaka et al. [15] in 2009. This was based on a dye-sensitized solar cell architecture, with a thin layer of perovskite on mesoporous TiO_2 as electron collector, and exhibited only 3.8% power conversion efficiency. Such kind of solar cell was only stable for a few minutes, due to the use of a liquid corrosive electrolyte. Park et al. reported a 6.5% efficiency in 2011 [28] using the same dye-sensitized concept and employing perovskite nanoparticles on TiO_2 to serve as sensitizers for improved absorption over conventional dyes [16].

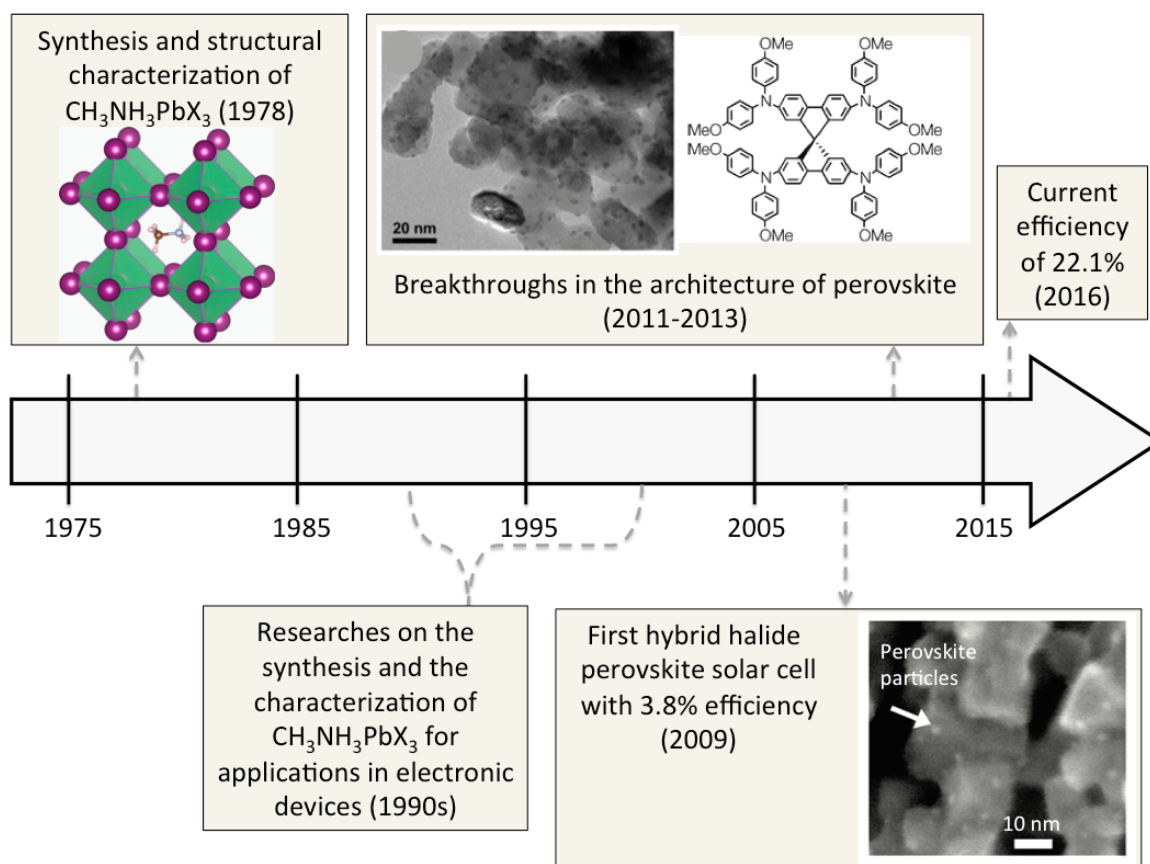


Figure 1.1: Timeline of research over structure, synthesis and optoelectronic properties of hybrid halide perovskite and important discoveries in the improvement of the perovskite solar cell efficiency.

Since 2012, enormous advances in HOIPs synthesis were reported. First, Henry Snaith and Mike Lee [29] from the University of Oxford found the perovskite to be stable when contacted with the solid electrolyte spiro-OMeTAD used as a hole transport material (HTM). An efficiency of 9.7% was achieved. A higher efficiency of 10.9% was attained by replacing the n-type TiO_2 electron transport material (ETM) with an inert Al_2O_3 scaffold [30]. It was then realized that $\text{CH}_3\text{NH}_3\text{PbI}_3$ can also act as the electron or hole conductor in planar

heterojunction cells [13]. In 2013, Henry Snaith et al. [31] fabricated flat heterojunction cells at low temperature with efficiencies of up to 11.4%; the first report of a fully thin-film perovskite solar cell with no mesoporous scaffold. In sensitized perovskite solar cells, the perovskite mainly acts as a light absorber and charge transport occurs in other materials. In contrast, in thin film solar cells, most electron or hole transport occurs in the perovskite itself. Both sensitized and planar architectures (shown in figure 1.2) reached an efficiency of more than 15% thanks to a two-step solution processing reported by Burschka et al. [32] and a thermal evaporation process reported by Liu et al. [33], respectively.

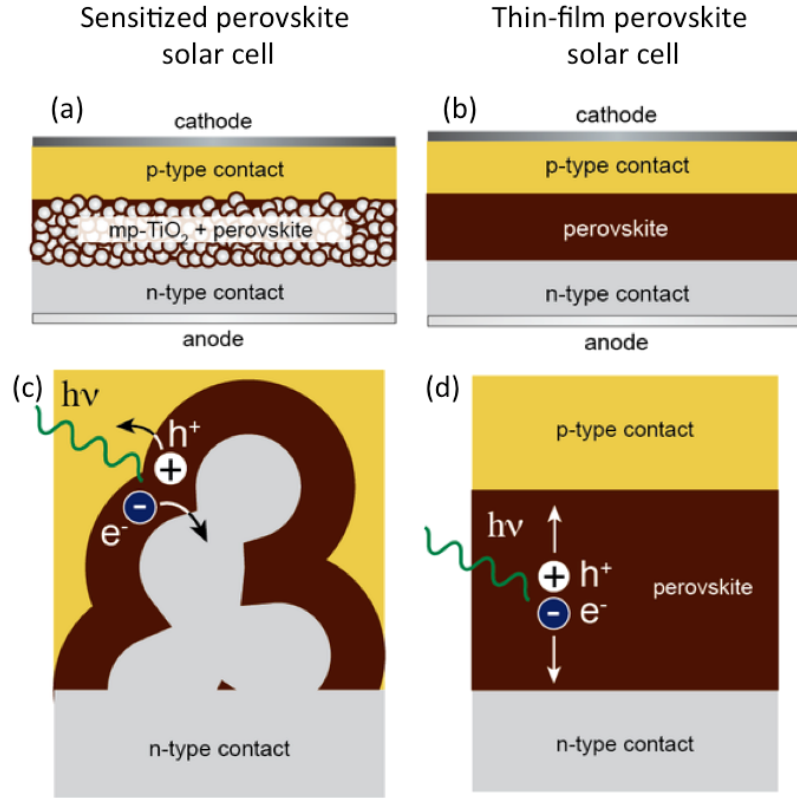


Figure 1.2: (a) Schematic of a sensitized perovskite solar cell. The active layer consists of mesoporous TiO₂ while the perovskite ensures the role of the absorber. The active layer is contacted with a n-type material for electron extraction and with a p-type material for hole extraction. (b) Schematic of a thin-film perovskite solar cell where the perovskite layer is contacted to a n-type and a p-type contacts. (c) Representation of the charge generation and extraction in a sensitized perovskite solar cell. Photons are absorbed in the perovskite absorber and the photogenerated electrons are injected and then extracted from the mesoporous TiO₂. (d) Representation of the charge generation and extraction in a thin-film perovskite solar cell. After light absorption, both electrons and holes are generated and extracted from the perovskite layer. [2]

In August 2014, Yang Yang et al. measured efficiency up to 19.3% via a reverse bias scan for planar thin-film perovskites fabricated in air and from solution at low temperature [34]. In November 2014, the South Korean Team KRICT achieved a record with the certification of a non-stabilized efficiency of 20.1% [1]. In December 2015, researchers from EPFL achieved a new record efficiency of 21.0%, while the highest certified record for a single-junction perovskite solar cell was reported in March 2016 by KRICT and UNIST, with 22.1% efficiency [1].

At present, the majority of the research field is focused on methylammonium lead halides, $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$). The principal characteristic of these materials is a tunable band gap depending on the halide content. It is therefore possible to cover band gaps from 1.1 to 2.1 eV in the visible light range, favorable for photovoltaic applications. The most commonly used perovskite system, namely the methylammonium lead iodide $\text{CH}_3\text{NH}_3\text{PbI}_3$, is studied in this manuscript. The material is a semiconductor with a band gap of 1.5-1.6 eV [13] exhibiting a high conversion efficiency $> 20\%$. Upon photoexcitation, since the exciton binding energy is low (< 10 meV) [35], electron-hole pairs rapidly dissociate at room temperature, leading to free carriers [36]. The free carriers display diffusion lengths of over one micron, very high mobilities of $66 \text{ cm}^2/\text{V}$ [35], and low non-radiative recombination rates, allowing efficient electron extraction from $\text{CH}_3\text{NH}_3\text{PbI}_3$.

In parallel with the rapid technological advances, intense research has been directed toward understanding the mechanisms which are responsible for the excellent photovoltaic performance of $\text{CH}_3\text{NH}_3\text{PbI}_3$. More specifically, the structural, electronic and vibrational properties have been studied by several work groups.

The structure of the methylammonium lead iodide was first reported by Weber in 1978 [22]. The structural evolution from orthorhombic to tetragonal to cubic perovskite structures as a function of the temperature has been studied by several techniques including nuclear magnetic resonance (NMR) [37], calorimetry and infrared spectroscopy [38], single-crystal X-ray diffraction (XRD) [12, 39, 40], and dielectric spectroscopy [41]. O.J. Weber et al. [42] reported recently a more quantitative insight into the temperature-dependent structural evolution of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thanks to powder neutron diffraction (PND) measurements. Several works of Marina R. Filip et al. [43–46] also focused on the electronic properties of other metal-halide perovskites by tuning the organic part of the system. Besides, M.H. Du [14] reported results for mixed halide $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ and compared their transport properties with the ones of $\text{CH}_3\text{NH}_3\text{PbI}_3$. Finally, toxicity concerns have also been addressed in order to find alternatives to Pb, such as Sn-based mixed halide perovskite solar cells [9]. Unfortunately, so far the highest conversion efficiency is only achieved in Pb-based perovskite solar cells.

It is well known that the band gap of material is not properly described by calculations based on LDA or GGA approximations used for the exchange-correlation term in the density functional theory (cfr. section 3). Weiwei Gao et al. [8] provided a clear understanding of the quasiparticle self-energy and spin-orbit coupling effects on the electronic properties. They also mentioned the role of organic molecules without structural distortions. More recently, in 2014, Marina R. Filip and Feliciano Giustino [9] studied the quasiparticle band gap of the hybrid organic-inorganic lead halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$, using many-body perturbation theory based on the GW approximation. They analyzed the band gap sensitivity to relativistic spin-orbit effects, to the description of semicore Pb-5d and I-4d electrons, and to the starting Kohn-Sham eigenvalues. Fan Zheng et al. [47] provided some ways to optimize the material performance by enhancing carrier lifetime thanks to Rashba spin-orbit effects.

What concerns the vibrational properties, Henry Snaith et al. [48] as well as Edoardo Mosconi et al. [49] both addressed computational studies of the vibrational spectra by performing density functional perturbation theory calculations. In 2015, Marina R. Filip et al. [13] provided a comprehensive group-theoretical analysis of the normal modes of vibration and predicted the infrared (IR) and Raman activity of each mode. In 2016, Aron Walsh et al. [50] calculated the phonon dispersion in each phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$ using the density functional theory. Moreover, A. Mattoni et al. [19] studied the temperature evolution of vibrations of $\text{CH}_3\text{NH}_3\text{PbI}_3$ by combining first principles and classical molecular dynamics.

Chapter 2

Perovskite structure and synthesis

2.1 Structure

Organometal hybrid perovskite materials exhibiting the ABX_3 form (with A: organic cations, B: lead or tin atoms, and X: halogens) have emerged as one of the most promising light absorbers and carrier transporters for thin-film solar cell applications. Among organic-inorganic perovskite materials, the methylammonium lead iodide $CH_3NH_3PbI_3$ has been shown to display unusual electronic and photoconductive properties ideal for photovoltaic applications. Methylammonium lead iodide was first described by Weber in 1978 [22]. In the $CH_3NH_3PbI_3$ perovskite structure, the Pb and I atoms form a three dimensional network of corner-sharing octahedra, with the Pb atoms occupying the center of each octahedron and the I atoms located at its corners [9]. In this configuration, the $CH_3NH_3^+$ cation is located at the center of a cuboctahedral cavity formed of corner-sharing PbI_6^- octahedra (see figure 2.1).

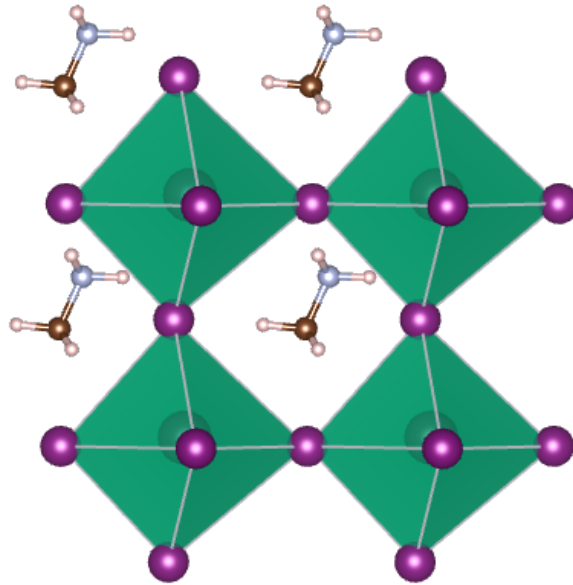


Figure 2.1: Polyhedral representation of the crystal structure of $CH_3NH_3PbI_3$. The atoms are respectively: Pb (in grey) located at the center of each octahedron, I (in purple) at the corners of each octahedron, C (in light blue), N (in brown) and H (in pink). For $CH_3NH_3^+$ cations, a ball-and-stick model is used.

The hybrid halide perovskite $CH_3NH_3PbI_3$ exhibits a complex structural behavior with several phase transitions.

At low temperature, $CH_3NH_3PbI_3$ crystallizes in an orthorhombic structure (figure 2.2(a)).

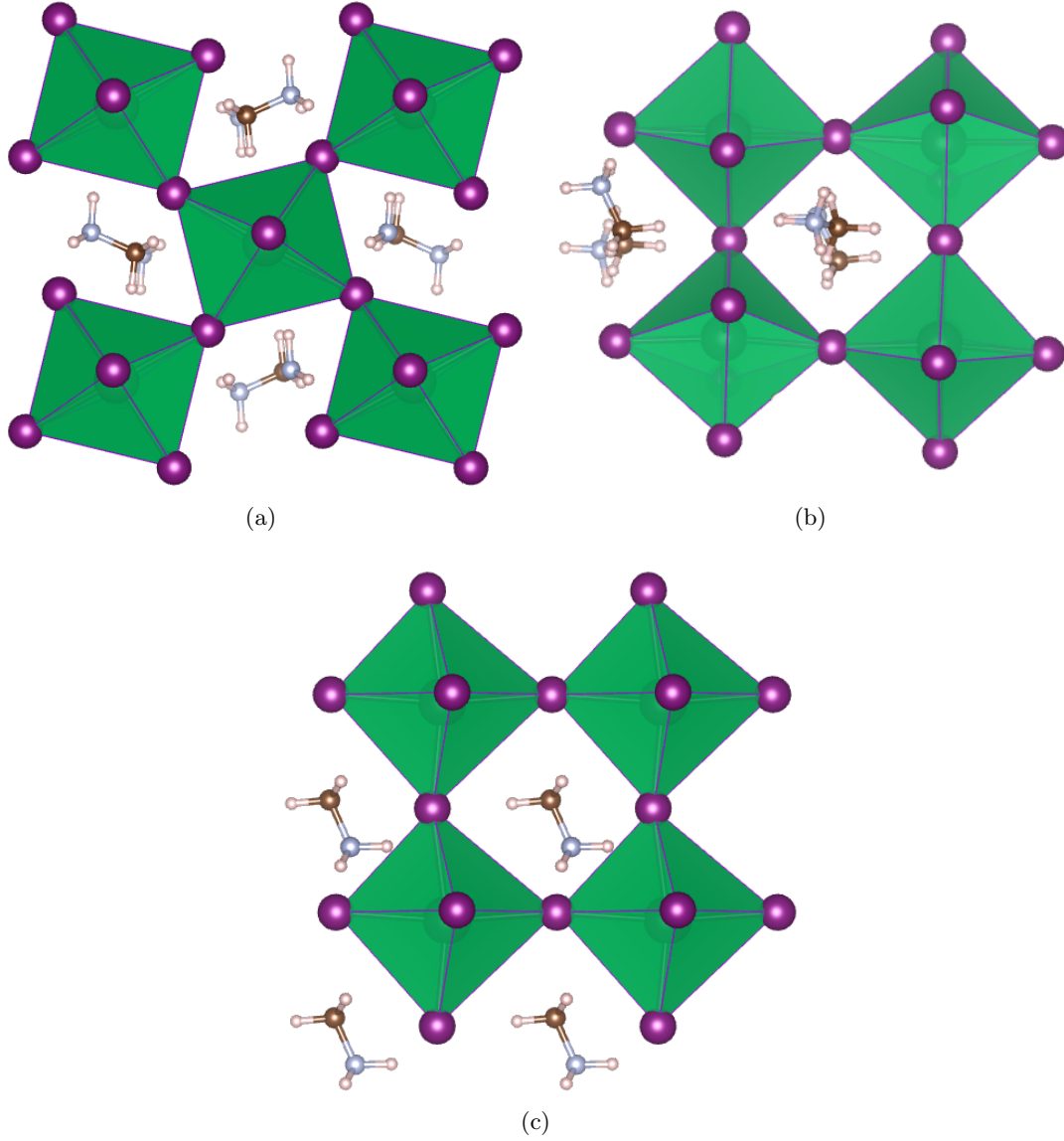


Figure 2.2: Polyhedral representation of the different polymorphs for the organic-inorganic halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$, depending on the temperature: (a) Orthorhombic ($Pnma$) structure stable for $T < 162.2\text{ K}$, (b) Tetragonal structure ($I4/mcm$) stable for $162.2 \leq T < 327.4\text{ K}$, (c) Cubic structure ($Pm\bar{3}m$) stable for $T \geq 327.4\text{ K}$. Atoms are represented as spheres: Pb are in grey and located at the center of each octahedron, I are in purple at the corners of each octahedron, C are in light blue, N are in brown, and H are in pink. For methylammonium cations, a ball-and-stick model is used.

In this low-temperature phase, the CH_3NH_3^+ cations have a well-defined orientation. Recently, a high-quality powder neutron diffraction (PND) analysis assigned the orthorhombic structure to $Pnma$ (a D_{2h} point group) [42].

Above 162.2 K , $\text{CH}_3\text{NH}_3\text{PbI}_3$ undergoes a first-order phase transition from the orthorhombic to the tetragonal (figure 2.2(b)) space group $I4/mcm$ (D_{4h} point group) [12]. While the configuration of the CH_3NH_3^+ cations is well-defined in the orthorhombic structure, there exists a considerable degree of angular fluctuations in the tetragonal phase.

As the temperature increases, the CH_3NH_3^+ cations become more orientationally disordered and a second-order phase transition occurs around 327.4 K to a most symmetric cubic (figure 2.2(c)) perovskite structure [12]. The space group of this structure is $Pm\bar{3}m$ (O_h

symmetry). The powder neutron diffraction analysis [42] revealed these rapid disorientation motions of CH_3NH_3^+ as the temperature increases. Kawamura et al. [39] studied the tetragonal to cubic transition by means of single crystal X-ray diffraction and confirmed the increase of the rotational angle of the octahedron from the tetragonal to the cubic phase. Moreover, an analysis of the real part of the dielectric permittivity revealed a discontinuity at the orthorhombic to tetragonal transition, but no apparent change around 327.4 K, confirming that the orthorhombic phase is completely ordered while both other phases are fully disordered [41, 51].

As atomic simulations within periodic boundary conditions require an ordered configuration, in this work *ab initio* calculations are done for the orthorhombic phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$.

2.2 Synthesis

Besides the excellent photovoltaic performance of the organic-inorganic perovskite, perovskite solar cells hold an advantage over traditional silicon solar cells in the simplicity and the versatility of their processing. Traditional silicon cells require very specific conditions for their processing: high temperatures above 1000°C, a high vacuum, and a lot of steps, making their production very expensive. For perovskite solar cells, whose performance is mainly attributed to the high-quality of the synthesized material, simple chemistry techniques in traditional laboratories can be used.

There are several deposition methods available for perovskite films, classified into two categories: solvent techniques including one-step precursor solution deposition [30] and two-step sequential deposition [32], and vapor deposition techniques including dual-source vapor deposition [33] and vapor-assisted solution process [34]. The main advantage of these techniques is that they can be scaled up with relative feasibility.

In solution processing, a lead halide and a methylammonium halide are dissolved in a solvent and spin coated onto a substrate. More precisely, in the one-step precursor solution deposition [30], the lead halide and the methylammonium halide are dissolved in dimethylformamide (DMF) or dimethylacetamide (DMA). The mixture is then spin-coated on top of a 200-400 nm-thick film of TiO_2 particles and maintained at higher temperature (figure 2.3). It leads to an ultra-smooth film of perovskite crystals up to 1 mm grain size [2].

In the two-step sequential deposition [32], the PbI_2 is first spin-coated on a mesoporous TiO_2 film reacts with the methylammonium iodide solution (figure 2.3). Lee and Park [4] reported a two-step deposition process improving the quality of the perovskite layer and leading to high-efficiency perovskite solar cells.

Figure 2.4 illustrates both procedures for the one-step and two-step spin-coating methods.

In the dual-source vapor deposition [33], the perovskite layer is deposited using a dual source sublimation method. The perovskite layer then acts as the electron donor in combination with an electron acceptor which is [6,6]-phenyl C_{61} -butyric acid methylester (figure 2.3). The organic materials are deposited using solution-based processes, whereas the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite is deposited using thermal evaporation under vacuum. The final device made by such kind of process reaches an efficiency of about 12%.

The vapor-assisted solution process was first reported by Yang et al. [34] and consists in a low-temperature approach combining the sequential deposition method and the dual-source vapor deposition [52]. Firstly, a PbI_2 film is deposited onto a substrate. Secondly, the structure is annealed in methylammonium iodide vapor at 150°C in a nitrogen atmosphere for two hours (figure 2.3). It gives rise to a thin perovskite film.

Sessolo et al. [53] reported some strategies in the vacuum deposition of perovskite films used in photovoltaic applications. Such vacuum deposition methods allow better control over

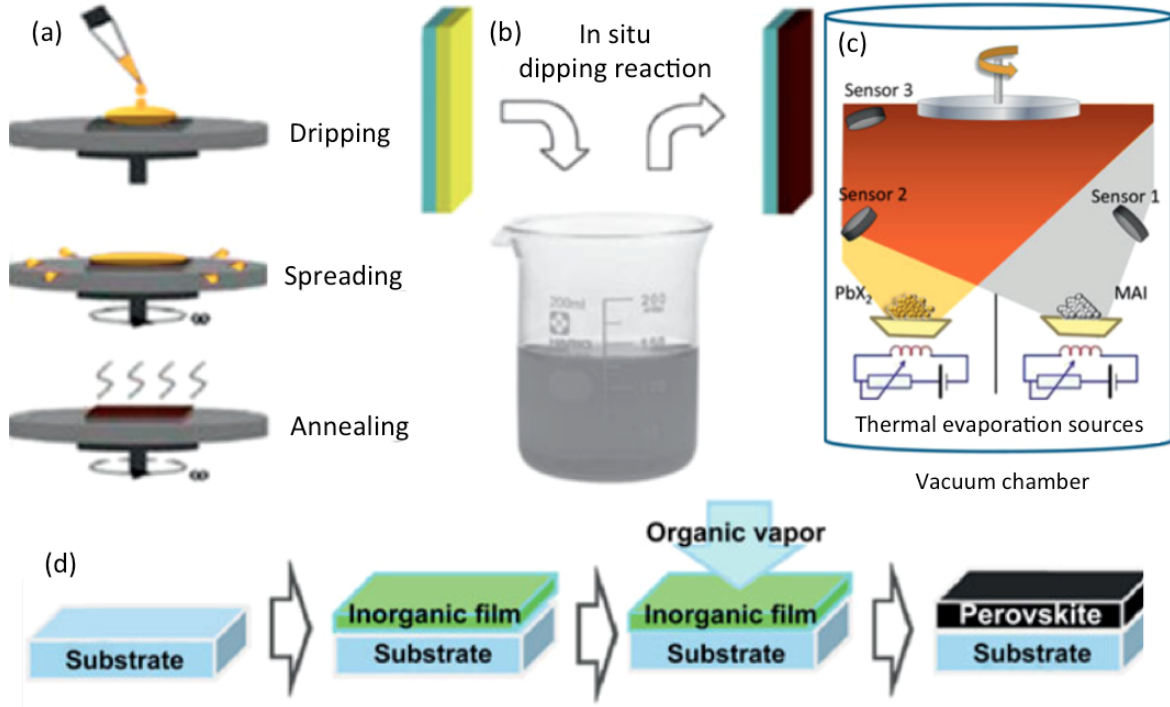


Figure 2.3: Main deposition methods to prepare perovskite active layers: (a) One-step precursor deposition, (b) two-step sequential deposition method, (c) dual-source vapor deposition, and (d) vapor-assisted solution process [3].

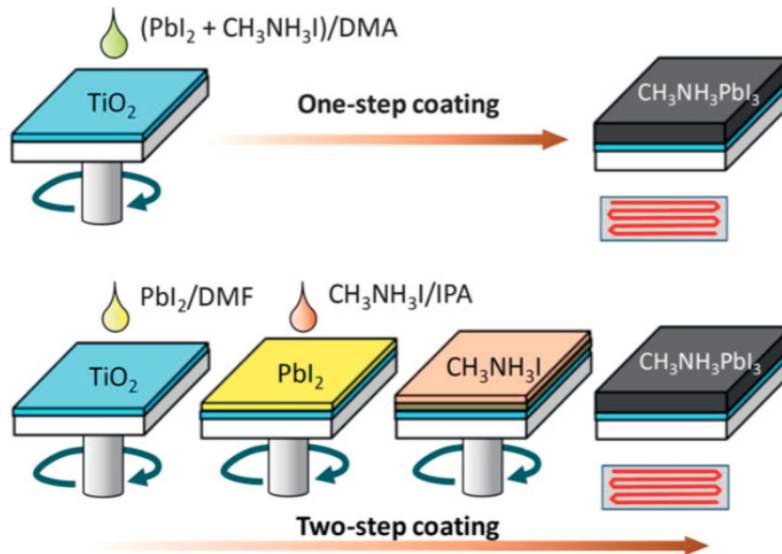


Figure 2.4: Schematic of one-step and two step coating methods to deposit $CH_3NH_3PbI_3$ perovskite thin films. For the one-step procedure, a single precursor solution containing the lead halide PbI_2 and the methylammonium halide CH_3NH_3I is used. For the two-step coating method, the methylammonium iodide solution reacts with the initially spin-coated PbI_2 film. DMA refers to dimethylacetamide, DMF to dimethylformamide and IPA to isopropyl alcohol. [4]

the film thickness, homogeneity, crystallinity and composition and can be performed at lower temperature. Zhou et al. [54] also discussed vapor-assisted solution processes including the

deposition of the inorganic framework by solution first and the subsequent in situ reaction between the inorganic species and the organic vapor. Thin film perovskites deposited by vapor-assisted solution process exhibit a power conversion efficiency up to 16.8%.

The greatest advantage of vapor assisted techniques over solution processing is that they reduce the need for use of further solvents reducing the risk of solvent remnants [3]. However, solution processing is cheaper.

Nowadays, research is mainly devoted to the stability issue of perovskite solar cells, as the material is observed to degrade in air, reducing the efficiency of the solar cell [3].

Chapter 3

Theoretical background

This chapter aims to quickly recall the foundations required to understand the vibrational and transport properties in solids, and more precisely in hybrid halide perovskites. The phonon spectrum can be obtained from experimental measurements but also from a theoretical approach and simulation. This second way is chosen for this work.

At first, the goal of section 3.1 is to introduce the theoretical framework of *ab initio* calculations, starting from the Schrödinger equation [55]. Different approximations needed to solve this many-body problem will be presented, such as the Born-Oppenheimer, the Hartree and the Hartree-Fock approximations [56].

Secondly, in section 3.2, it will be shown how the Schrödinger equation can be solved thanks to the Density Functional Theory (DFT); which is one of the most commonly used methods to solve *ab initio* problems [57]. One of the major parts of this work is devoted to the study of the effects involved by the implementation of van der Waals interactions in solid state systems. Therefore, this section will also focus on the development of approximate exchange-correlation energy functionals that accurately model the physically and chemically very important London dispersion interactions [58].

In section 3.3, some practical considerations for solid state systems are mentioned in order to perform feasible numerical simulations.

Section 3.4 will present the extension of the DFT to perturbed systems, that is the Density Functional Perturbation Theory (DFPT) [59]. From this theory, it will be shown how the response function properties can be obtained, for different kinds of perturbations: electric field, atomic displacements,... More specifically, phonons, dielectric permittivities and Born-effective charges will be discussed [5].

Finally, section 3.5 will quickly introduce the theoretical notions related to spin-orbit coupling [5, 60].

3.1 Schrödinger equation and the many-body problem

This section is mainly based on "MAPR 1492: Physique des matériaux" taught by Prof. G.-M. Rignanese [55].

3.1.1 Born-Oppenheimer approximation

Let us consider a crystalline solid system constituted of N_e electrons and N_N nuclei, the system is completely quantum-mechanically described by its wave function Ψ :

$$\Psi = \Psi(r_1, r_2, \dots, r_{N_e}, R_1, R_2, \dots, R_{N_N}) \quad (3.1)$$

where r_i ($i = 1, \dots, N_e$) and R_α ($\alpha = 1, \dots, N_N$) are the coordinates of electrons and nuclei, respectively. The square of the amplitude of this wave function gives the density of probability to find a particular configuration of electrons and nuclei. The accurate description

of a non-relativistic system requires a quantum approach and the resolution of the so-called Schrödinger equation. The stationary Schrödinger equation is given by:

$$\hat{H}\Psi = E\Psi \quad (3.2)$$

where $\hat{H}$ is the Hamiltonian operator defined by:

$$\hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{ee} + \hat{V}_{eN} + \hat{V}_{NN} \quad (3.3)$$

These operators correspond to:

$$\begin{aligned} \hat{T}_e &= \sum_{i=1}^{N_e} -\frac{1}{2} \nabla_{r_i}^2, & \text{the electronic kinetic energy} \\ \hat{T}_N &= \sum_{\alpha=1}^{N_N} -\frac{1}{2M_\alpha} \nabla_{R_\alpha}^2, & \text{the nuclear kinetic energy} \\ \hat{V}_{ee} &= \sum_{i,j;i < j}^{N_e, N_e} \frac{1}{|r_i - r_j|}, & \text{the electron-electron Coulomb interaction} \\ \hat{V}_{eN} &= \sum_{i=1}^{N_e} \sum_{\alpha=1}^{N_N} \frac{-Z_\alpha}{|r_i - R_\alpha|}, & \text{the electron-nucleus Coulomb interaction} \\ \hat{V}_{NN} &= \sum_{\alpha, \beta; \alpha < \beta}^{N_N, N_N} \frac{Z_\alpha Z_\beta}{|R_\alpha - R_\beta|}, & \text{the nucleus-nucleus Coulomb interaction} \end{aligned}$$

As the nuclei are much heavier, hence slower, than the electrons, the Born-Oppenheimer approximation states that the nuclei positions are fixed and that electrons almost instantaneously conform to the nuclei configuration. Hence, the wave function of the system can be split into its electronic and nuclear components:

$$\Psi = \Psi^e(r_1, r_2, \dots, r_{N_e}) \Psi^N(R_1, R_2, \dots, R_{N_N}) \quad (3.4)$$

The electron position can be obtained, for a fixed nuclei configuration, by solving the time-independent Schrödinger equation:

$$\hat{H}_{\{R\}}^e \Psi^e(r_1, r_2, \dots, r_{N_e}) = E_{\{R\}}^e \Psi^e(r_1, r_2, \dots, r_{N_e}) \quad (3.5)$$

$$\hat{H}_{\{R\}}^e = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} \quad (3.6)$$

The nucleus-electron Coulomb interaction is often denoted as the external potential $V_{\text{ext}}(r_i)$ and the Schrödinger equation simplifies to:

$$\hat{H}_{\{R\}}^e \Psi^e = \sum_{i=1}^{N_e} \left(-\frac{1}{2} \nabla_i^2 + V_{\text{ext}}(r_i) + \sum_{i,j;i < j}^{N_e, N_e} \frac{1}{|r_i - r_j|} \right) \Psi^e = E_{\{R\}}^e \Psi^e \quad (3.7)$$

Treatment of nuclei

In contrast with the case of electrons, where a quantum approach is mandatory, the nuclei dynamic is generally described from a classical point of view [5]. An electronic energy is reintroduced as a potential energy of interaction between nuclei, $E_{\{R\}}^e$, which takes the instantaneous rearrangement of electrons into account. The force in direction α ($\alpha = 1, 2, 3$) is given by:

$$F_\alpha = -\nabla_{R_\alpha} \left(\hat{V}_{NN} + E_{\{R\}}^e \right) \quad (3.8)$$

In a perfect periodic crystal, each atom κ in the cell a is characterized by a mass M_κ and its position is given by the vector $R_{\kappa\alpha}^a$ in the direction α :

$$R_{\kappa\alpha}^a = R_\alpha^a + \tau_\alpha^a + u_{\kappa\alpha}^a \quad (3.9)$$

where R_α^a is the position of the cell a , τ_α^a is the equilibrium position of atom κ inside the cell a and $u_{\kappa\alpha}^a$ is the displacement around its equilibrium position. In order to determine the equilibrium position of each atom, equation 3.10 must be solved with $E_{\text{tot}} = E_{\text{ion}} + E_{\text{el}}$, the total energy of the system.

$$F_{\kappa\alpha}^a = - \left. \frac{\partial E_{\text{tot}}}{\partial R_{\kappa\alpha}^a} \right|_{\{R\}} = M_\kappa \frac{d^2 R_{\kappa\alpha}^a}{dt^2} \quad (3.10)$$

3.1.2 Wave function methods

Equation 3.7 cannot be solved analytically for more than two electrons. One observes an exponential explosion problem [56] and the problem becomes too complex due to the treatment of the electron-electron Coulomb interaction. A first approximation consists in neglecting it and considering electrons as non-interacting electrons. Equation 3.7 simplifies to:

$$\sum_{i=1}^{N_e} \left(-\frac{1}{2} \nabla_{r_i}^2 + \sum_{\alpha=1}^{N_N} \frac{-Z_\alpha}{|r_i - R_\alpha|} \right) \Psi^e = E_{\{R\}}^e \Psi^e \quad (3.11)$$

In order to satisfy Pauli exclusion principle, which states that "the wave function of an electronic system is antisymmetric regarding the permutation of spin-space coordinates of any pair of particles" [61], Slater proposed to represent the wave function as a determinant:

$$\Psi^e(r_1, r_2, \dots, r_{N_e}) = \frac{1}{\sqrt{N_e!}} \begin{vmatrix} \phi_1(r_1) & \phi_2(r_1) & \cdots & \phi_{N_e}(r_1) \\ \phi_1(r_2) & \phi_2(r_2) & \cdots & \phi_{N_e}(r_2) \\ \vdots & \vdots & & \vdots \\ \phi_1(r_{N_e}) & \phi_2(r_{N_e}) & \cdots & \phi_{N_e}(r_{N_e}) \end{vmatrix} \quad (3.12)$$

One direct consequence of such a representation is the impossibility for two electrons to occupy the same spinorbital [61]. The wave functions $\phi_j(r_i)$ in equation 3.12 are the solutions of the eigenvalue problem:

$$\left(-\frac{1}{2} \nabla^2 + V_{\text{ext}}(r_i) \right) \phi_j(r_i) = \varepsilon_j \phi_j(r_i) \quad (3.13)$$

and satisfy the orthonormalization condition $\langle \phi_i | \phi_j \rangle = \delta_{ij}$.

Given the simplification of equations, it is interesting to keep the formalism of independent electrons while reintroducing some interaction between electrons. It can be done by introducing a potential judiciously selected $U(r)$:

$$\begin{aligned} \hat{H}_{\{R\}}^e &= -\frac{1}{2} \nabla_r^2 + \sum_{\alpha=1}^{N_N} \frac{-Z_\alpha}{|r - R_\alpha|} + \hat{U}(r) \\ &= -\frac{1}{2} \nabla_r^2 + \hat{V}_{\text{eff}}(r) \end{aligned} \quad (3.14)$$

where $V_{\text{eff}}(r)$ is the mean-field potential.

Different models try to approximate the effective potential $V_{\text{eff}}(r)$ such as the Hartree model, the Hartree-Fock model and some approximations to the Density Functional Theory (DFT).

Hartree approximation

The Hartree approximation [62] assumes that the wave function of a many-body system can be approximated by the product of N_e mono-electronic wave functions, even when the electron-electron interactions are not neglected.

$$\Psi^e(r_1, r_2, \dots, r_{N_e}) = \phi_1(r_1) \phi_2(r_2) \dots \phi_{N_e}(r_{N_e}) \quad (3.15)$$

This wave function is only an approximation of the real wave function and is far simpler.

The best solution, according to the variational principle (the one minimizing the total energy) is a solution of:

$$\left[-\frac{1}{2} \nabla_i^2 + \sum_{\alpha=1}^{N_N} \frac{-Z_\alpha}{|r_i - R_\alpha|} + \sum_{j \neq i} \hat{J}_j \right] \phi_i(r_i) = \varepsilon_i \phi_i(r_i) \quad (3.16)$$

where $\hat{J}_j$ is the Coulomb operator defined by:

$$\hat{J}_j \phi_i(r_j) = \left[\int \frac{\phi_j^*(r_j) \phi_j(r_j)}{|r_i - r_j|} \right] \phi_i(r_j) \quad (3.17)$$

In the Hartree model, the mean-field potential $V_{\text{eff}}(r)$ is thus approximated as the sum of the external potential $V_{\text{ext}}(r)$ and the electro-static potential generated by all the electrons (seen as an electronic cloud) $V_H(r)$ defined by:

$$V_H(r) = \int \frac{\rho(r')}{|r - r'|} dr' \quad (3.18)$$

where $\rho(r)$ is the electronic density defined as:

$$\rho(r) = \sum_{i=1}^{N_e} |\phi_i(r)|^2 \quad (3.19)$$

When including the self-interaction, equation 3.16 can rewrite as:

$$\left[-\frac{1}{2} \nabla^2 + V_{\text{ext}}(r) + V_H(r) \right] \phi_i(r) = \varepsilon_i \phi_i(r) \quad (3.20)$$

In order to determine the Hartree potential $V_H(r)$, the electronic density and hence the wave functions $\phi_i(r_j)$ are needed and to obtain the wave functions $\phi_i(r_j)$, the Hartree potential $V_H(r)$ is required. In practice, equation 3.18, 3.19, and 3.20 are solved iteratively: one starts from a trial electronic density and then iterates until self-consistency is reached.

Unfortunately, two quantum effects are not taken into account in this model: an exchange term due to the presence of an additional repulsive interaction between two electrons of same spin, and a term including the correlation between electrons. These terms are both correctly described in density functional approximations as it will be shown in section 3.2. Moreover the wave function in equation 3.15 does not respect Pauli exclusion principle as it is not antisymmetric. The Hartree-Fock approximation solves this problem [56, 61].

Hartree-Fock approximation

In order to satisfy Pauli exclusion principle, the wave function should be replaced by a Slater determinant, as suggested by V. Fock:

$$\Psi^e(r_1, r_2, \dots, r_{N_e}) = \frac{1}{\sqrt{N_e!}} \begin{vmatrix} \phi_1(r_1) & \phi_2(r_1) & \cdots & \phi_{N_e}(r_1) \\ \phi_1(r_2) & \phi_2(r_2) & \cdots & \phi_{N_e}(r_2) \\ \vdots & \vdots & & \vdots \\ \phi_1(r_{N_e}) & \phi_2(r_{N_e}) & \cdots & \phi_{N_e}(r_{N_e}) \end{vmatrix} \quad (3.21)$$

The Hartree-Fock approximation is based on the representation of the wave function of the ground state in the form of a Slater determinant and on the optimization of this one by using the variational approach [61]. The Hartree-Fock equation in its canonical form shows a sum over the N_e occupied spinorbitals:

$$\left[-\frac{1}{2}\nabla_r^2 + V_{\text{ext}}(r) + \sum_{j=1}^{N_e} \left(\hat{J}_j(r) - \hat{K}_j(r) \right) \right] \phi_i(r) = \varepsilon_i^{\text{HF}} \phi_i(r) \quad (3.22)$$

where $\hat{J}_j(r)$ is the Coulomb operator and $\hat{K}_j(r)$ is the exchange operator. $\hat{J}_j(r)$ is defined by:

$$\hat{J}_j(r)\phi_i(r) = \int \frac{\phi_j^*(r')\phi_j(r')}{|r-r'|} dr' \phi_i(r) \quad (3.23)$$

and describes the average coulombian repulsive potential associated to the electronic density. This operator is said local because it does not depend on the spinorbital on which it acts. $\hat{K}_j(r)$ is defined by:

$$\hat{K}_j(r)\phi_i(r) = \int \frac{\phi_j^*(r')\phi_i(r')}{|r-r'|} dr' \phi_j(r) \quad (3.24)$$

and has a quantum origin. It comes from the antisymmetric nature of the Slater determinant. This operator is said non-local because it depends on the spinorbital on which it acts.

Equation 3.22 can be seen as an eigenvalue problem:

$$\hat{F}(r)\phi_i(r) = \varepsilon_i\phi_i(r) \quad (3.25)$$

when defining the Fock operator $\hat{F}(r)$:

$$\hat{F}(r) = -\frac{1}{2}\nabla^2 + \sum_{\alpha=1}^{N_N} \frac{-Z_{\alpha}}{|r-R_{\alpha}|} + \sum_{j=1}^{N_e} \left(\hat{J}_j(r) - \hat{K}_j(r) \right) \quad (3.26)$$

Again, this eigenvalue problem is solved iteratively as $\hat{F}(r)$ depends on the wave functions.

Thereafter, numerous methods referred to as post-Hartree-Fock methods have been developed in order to improve the description of the wave function and the accuracy of the numerical simulations. These methods include an electron correlation that is not taken into account in the Hartree-Fock method.

3.2 Density functional theory

The Hartree-Fock method does not describe properly the electronic energies while post-Hartree-Fock methods have a calculation time which quickly explodes with the system size.

Hohenberg, Kohn and Sham enounced the Density Functional Theory (DFT) [63, 64] based on the idea that only the electronic density is required to determine all the properties of the ground-state. This theory provides a proof that there exists an exact V_{eff} , which is unfortunately unknown.

This section is mainly based on "*CHIM1353: Chimie quantique*" taught by Prof. G. Hautier [56].

3.2.1 Hohenberg-Kohn theorems

Let us consider all possible Schrödinger equations for N_e electrons which only differ by the external potential $V_{\text{ext}}(r)$ [65]:

$$\hat{H}\Psi = \left[-\frac{1}{2} \sum_{i=1}^{N_e} \nabla_i^2 + \sum_{i=1}^{N_e} V_{\text{ext}}(r_i) + \sum_{i,j;i < j}^{N_e, N_e} \frac{1}{|r_i - r_j|} \right] \Psi = E\Psi \quad (3.27)$$

For a given external potential $V_{\text{ext}}(r)$, it is possible to find the ground-state wave function and hence the electronic density. Hohenberg and Kohn have demonstrated that: whatever the system of interacting particles in an external potential $V_{\text{ext}}(r)$, this potential is uniquely determined (modulo a global constant) by the electronic density of the ground-state $\rho(r)$ defined by [56]:

$$\rho(r) = N_e \int [\Psi(r, r_2, \dots, r_{N_e})]^* \Psi(r, r_2, \dots, r_{N_e}) dr_2 \dots dr_{N_e} \quad (3.28)$$

Moreover, if the arbitrary constant for the external potential is fixed, the total electronic energy is also a functional of the density:

$$\rho(r) \Rightarrow V_{\text{ext}}(r) \Rightarrow \hat{H} = \hat{T} + \hat{V}_{ee} + V_{\text{ext}} \Rightarrow \Psi \Rightarrow E = \langle \Psi | \hat{H} | \Psi \rangle = E[\rho] \quad (3.29)$$

Indeed, the Hamiltonian is uniquely determined by specifying the external potential (or the density). According to the variational principle, the energy functional of the electronic density can be expressed by:

$$\begin{aligned} E[\tilde{\rho}] &= \langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = \langle \tilde{\Psi} | \hat{T}_e + \hat{V}_{ee} + V_{\text{ext}} | \tilde{\Psi} \rangle \\ &= \int \tilde{\rho}(r) V_{\text{ext}}(r) dr + F_{\text{HK}}[\tilde{\rho}] \end{aligned} \quad (3.30)$$

and the ground-state energy is given by:

$$E_0[\rho_0] = \min \{E[\tilde{\rho}]\} = \int \rho_0(r) V_{\text{ext}} dr + F_{\text{HK}}[\rho_0] \leq E[\tilde{\rho}] \quad (3.31)$$

with $\tilde{\Psi}$, a trial wave function and $\tilde{\rho}$, the corresponding trial electronic density. The first term in equation 3.30 is an electro-static interaction between the electronic density and the external potential, and $F_{\text{HK}}[\tilde{\rho}]$ includes the more complex part, that is the kinetic energy, and the electron-electron interactions (exchange and correlation). $F_{\text{HK}}[\tilde{\rho}]$ is a universal functional of the density, but is unfortunately not known explicitly.

The second Hohenberg-Kohn theorem states that: a universal functional of the density can be defined for any given external potential. For a given external potential, the exact energy of the ground-state E_0 corresponds to the global minimum of this functional. The density minimizing this functional is the exact fundamental density ρ_0 [56].

$F_{\text{HK}}[\tilde{\rho}]$ represents an important part of the total electronic energy and it is therefore mandatory to make a reasonable approximation of $F_{\text{HK}}[\tilde{\rho}]$ in order to obtain good result for the energy of the ground-state.

3.2.2 Kohn-Sham equations

Kohn and Sham established a connection between a system of interacting electrons and a system of non-interacting electrons with the same electronic density:

$$F_{\text{HK}}[\rho] = T_{\text{KS}}[\rho] + E_{\text{H}}[\rho] + E_{\text{xc}}[\rho] \quad (3.32)$$

with

$$T_{\text{KS}}[\rho] = \min_{\Psi \rightarrow \rho} \left\{ \langle \Psi | \hat{T}_e | \Psi \rangle \right\}, \quad \text{known kinetic energy functional of the density}$$

$$E_{\text{H}}[\rho] = \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r - r'|} dr dr', \quad \text{Hartree energy}$$

$$E_{\text{xc}}[\rho] = F_{\text{HK}}[\rho] - T_{\text{KS}}[\rho] - J[\rho], \quad \text{exchange-correlation energy functional}$$

$E_{\text{xc}}[\rho]$ contains an exchange term, a correlation term and the difference between the kinetic energies of the systems of interacting and non-interacting electrons [65]. The system can be seen as a system of non-interacting electrons with the same electronic density in an external potential called the Kohn-Sham potential $V_{\text{KS}}(r)$:

$$V_{\text{KS}}(r) = V_{\text{ext}}(r) + V_{\text{H}}[\rho] + V_{\text{xc}}(r) \quad (3.33)$$

where V_{H} is the Hartree potential and $V_{\text{xc}}(r)$ is the exchange-correlation potential defined by:

$$V_{\text{xc}}(r) = \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho} \quad (3.34)$$

In order to obtain the total energy and the electronic density, one has to solve self-consistently the following equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{KS}}(r) \right] \phi_i^{\text{KS}}(r) = \varepsilon_i^{\text{KS}} \phi_i^{\text{KS}}(r) \quad (3.35)$$

with the electronic density:

$$\rho(r) = \sum_{i=1}^{N_e} |\phi_i^{\text{KS}}(r)|^2 \quad (3.36)$$

The challenge of DFT methods is the modelization of the exchange-correlation potential. If it was exactly determined, the electronic density and hence the total energy would be the exact ones.

3.2.3 Functionals for exchange and correlation

It is possible to show that the exchange-correlation energy functional can be written as the integral over the whole space of the density multiplied by the local exchange-correlation energy per electron $\varepsilon_{\text{xc}}(r, \rho)$:

$$E_{\text{xc}}[\rho] = \int \rho(r) \varepsilon_{\text{xc}}(r, \rho) dr \quad (3.37)$$

The most important exchange-correlation functional approximations, the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA), are discussed in this work.

Local density approximation

The Local Density Approximation (LDA), introduced by Kohn and Sham in 1965 [64], assumes that the local exchange-correlation energy per electron corresponds to that of an homogeneous electron gas with the same density:

$$\varepsilon_{\text{xc}}^{\text{LDA}}(r, \rho) = \varepsilon_{\text{xc}}^{\text{hom}}(\rho(r)) \quad (3.38)$$

It only depends on the local density. Although LDA seems rather simple, it gives excellent numerical results, especially for vibrational and structural properties.

Generalized gradient approximation

The Generalized Gradient Approximation (GGA) does not only take the local density into account but also the gradients of this local density:

$$E_{\text{xc}}^{\text{GGA}}[\rho] = \int \rho(r) \varepsilon_{\text{xc}}(\rho(r), |\nabla \rho(r)|, \nabla^2 \rho(r)) dr \quad (3.39)$$

In opposition to LDA, there exist a variety of GGA exchange-correlation functionals. The Perdew-Burke-Ernzerhof formulation [66] is chosen for this work.

In general, GGA allows more accurate descriptions of systems than LDA.

The most notable problem with functionals (both LDA and GGA) is the band gap prediction, which systematically presents an error of about 30-50%.

Van der Waals interactions

The development of approximate exchange-correlation energy functionals [57] approaches that properly describe the physically and chemically van der Waals interactions is a very attractive field of research [67–70]. In order to reach the so-called chemical accuracy and to properly reproduce experimental results of weakly bonded (vdW) systems, these dispersive contributions have to be considered.

Actually, the most popular exchange-correlation functionals (i.e. LDA, GGA, and hybrid functionals), used for electronic structure calculations in condensed matter physics and quantum chemistry [64], do not take these long-range electron correlations into account. In order to properly describe vdW systems, different methods have been developed over the past years. Two main categories can be distinguished: the first one includes density-dependent methods while the second one includes simpler density-independent methods [71].

In the first category, the most prominent methods are the Tkatchenko-Scheffer van der Waals (TS-vdW) method [72] whose corrections to DFT include a term depending both on the geometry and on the electronic density of the system, vdW-DF methods [73–75] whose corrections to DFT include a long-range term to treat the dispersive effects, and the Silvestrelli approach [76, 77] whose corrections to the Kohn-Sham energy is evaluated by localized Wannier functions. The main disadvantage of these wave function-dependent methods is the implementation time that may be significant.

The second category is mainly devoted to Grimme’s DFT-D dispersive corrections [58, 78, 79]. Different variants of DFT-D methods have been proposed by S. Grimme and they all include corrections depending on the nuclei positions and on the exchange-correlation functional approximation in use. In contrast to other methods, in DFT-D, the computation time added by the inclusion of an energetic correction term including vdW interactions is negligible compared to the electronic Kohn-Sham DFT computation time [58]. DFT-D corrections play an important role for the ground-state geometry. Therefore, two effects can be distinguished when vdW interactions are taken into account for phonon calculations: an indirect effect related to the variation of the ground state geometry, and a direct effect related to the modification of the IFCs. Although the indirect effect is by far the principal origin of the change in phonon frequencies and eigenvalues, the corrections to the IFCs can not be neglected.

DFT-D approaches are based on Becke’s GGA functional introduced in 1997 [80]. The total energy of the system is given by:

$$E_{\text{DFT-D}} = E_{\text{KS-DFT}} - E_{\text{disp}} \quad (3.40)$$

where $E_{\text{KS-DFT}}$ is the usual Kohn-Sham energy obtained from a chosen DF and E_{disp} is a correction including vdW interactions. E_{disp} is given by:

$$E_{\text{disp}} = s_6 \sum_{i=1}^{N_{\text{at}}-1} \sum_{j=i+1}^{N_{\text{at}}} \frac{C_6^{ij}}{R_{ij}^6} f_{\text{dmp}}(R_{ij}) \quad (3.41)$$

with N_{at} the number of atoms in the system, C_6^{ij} the dispersion coefficient for atom pair ij , s_6 a global scaling factor only depending on the DF in use, and R_{ij} the interatomic distance [78]. The key ingredient of all DFT-D methods is the damping function f_{dmp} which determines the short-range behavior of the correction and is needed in order to avoid near-singularities for small R_{ij} and double-counting effects of electron correlation at intermediate distances [79].

The first DFT-D method proposed by S. Grimme in 2004 [81] has proved high accuracy in many different applications [78]. However, the main important shortcoming of this method is that consistent parameters C_6^{ij} and R_{ij} are only available for elements H, C-Ne and not for all elements from the periodic table.

In order to cover larger parts of the periodic table (up to Xenon), DFT-D1 has been improved in 2006 [78]. In contrast to DFT-D1 in which C_6^{ij} dispersion coefficients were given by a geometric mean:

$$C_6^{ij} = \sqrt{C_6^i C_6^j} \quad (3.42)$$

in DFT-D2, they are computed from a scheme based on the London formula for dispersion. Better agreement with experimental results is reached but the most fundamental drawback of this method is that dispersion coefficients are computed for each chemical pair of atoms and do not take the chemical environment, and hence the geometry, into account.

In DFT-D3 [58] developed in 2010, environment-dependent coefficients are used in order to get a better chemical accuracy. Moreover, a three-body term [82] can also be added and represents interactions between an atom, its neighbour and the next atom through induced dipolar interactions. The main modifications regarding the previous DFT-D2 method are the following: atom pair-wise dispersion coefficients C_n^{ij} and cut-off radii R_{ij}^0 - which determines in which interatomic distance region the dispersion energy is decreasing - are more accurate and are computed from first-principles, only two parameters are adjustable depending on the DF in use and the method is therefore less empirical, and finally consistent parameters are available for elements up to $Z=94$ [58]. It has to be noted that the largest part of the residual error is mainly due to the exchange-correlation approximation in use.

The total energy is now given by:

$$E_{\text{DFT-D3}} = E_{\text{KS-DFT}} - E_{\text{disp}} \quad (3.43)$$

with E_{disp} a dispersion correction including a two-body and a three-body terms:

$$E_{\text{disp}} = E^{(2)} + E^{(3)} \quad (3.44)$$

$$E^{(2)} = \sum_{i=1}^{N_{\text{at}}} \sum_{j=i+1}^{N_{\text{at}}} \sum_{n=6,8,10\dots} s_n \frac{C_n^{ij}}{R_{ij}^n} f_{\text{dmp},n}(R_{ij}) \quad (3.45)$$

The two first sum state for all atom pairs, C_n^{ij} are the averaged isotropic n^{th} -order dispersion coefficient ($n = 6, 8, 10\dots$) for atomic pair ij , R_{ij} are their internuclear distance, s_n are adjustable parameters for any DF [81] and $f_{\text{dmp},n}$ is the damping function. High-order terms are necessary to adapt the potential in the midrange region depending on the DF in use. It can be shown that only $n \leq 8$ terms are necessary as the $n > 8$ ones lead to instabilities. The s_8 factor is the first empirical parameter of the method. Besides, as it does not improve the results considerably, the three-body term is often neglected.

As previously mentioned, dispersion coefficients are now computed *ab initio* from first-principles. The starting point is the Casimir Polder formula [71, 83]:

$$C_6^{ij} = \frac{3}{\pi} \int_0^\infty \alpha^i(i\omega) \alpha^j(i\omega) d\omega \quad (3.46)$$

where $\alpha(i\omega)$ is the averaged dipole polarizability at imaginary frequency ω . The higher-order coefficients are computed by employing recursion relations [84] according to:

$$C_8^{ij} = 3C_6^{ij} \sqrt{Q^i Q^j} \quad (3.47)$$

where Q^i are tabulated values expressing the link between lower and higher dispersion coefficients [71]. In order to get environment-dependent dispersion coefficients, $\alpha(i\omega)$ should be computed for molecules with a well-defined electronic structure, instead of isolated atoms. Numerically simulated coefficients present a mean percentage deviation of only 8.4% compared to experimental coefficients, known from dipole oscillator strength distributions [58].

The atom pair-wise cut-off radii R_{ij}^0 determine in which interatomic distance region the dispersion energy is calculated and are computed from first-principles for all atom pair ij .

A typical expression for the damping function is [79]:

$$f_{\text{dmp},n}(R_{ij}) = \frac{1}{1 + 6 \left(\frac{R_{ij}}{s_{r,n} R_{ij}^0} \right)^{-\gamma_n}} \quad (3.48)$$

with R_{ij}^0 the cut-off radius for atom pair ij , $s_{r,n}$ functional-dependent radii scaling factor and γ_n parameters that determine the steepness of the function for small radii. The damping function approaches zero for $R_{ij} \rightarrow 0$.

Becke and Johnson (BJ) [85,86] proposed a more physical rational damping leading to a constant contribution of E_{disp} to the correlation energy for each atom pair, given by:

$$E_{\text{disp}} = \sum_{i=1}^{N_{\text{at}}-1} \sum_{j=i+1}^{N_{\text{at}}} \frac{C_6^{ij}}{R_{ij}^n + \text{Const}} \quad (3.49)$$

The revised DFT-D3 method, referred to as DFT-D3(BJ) shows a dispersion energy with the form:

$$E_{\text{disp}}^{\text{DFT-D3(BJ)}} = \sum_{i=1}^{N_{\text{at}}-1} \sum_{j=i+1}^{N_{\text{at}}} \left(s_6 \frac{C_6^{ij}}{R_{ij}^6 + [f(R_{ij}^0)]^6} + s_8 \frac{C_8^{ij}}{R_{ij}^8 + [f(R_{ij}^0)]^8} \right) \quad (3.50)$$

with $f(R_{ij}^0) = a_1 R_{ij}^0 + a_2$, a_1 and a_2 are fitted parameters introduced by BJ, and $R_{ij}^0 = \sqrt{\frac{C_8^{ij}}{C_6^{ij}}}$, s_6 is equal to 1 for GGA functionals and s_8 is an empirical parameter which can be adjusted depending on the exchange-correlation functional in use.

Compared to DFT-D3, DFT-D3(BJ) does not require pair-specific cut-off radii, but one additional fitting parameter is necessary.

3.3 Solid state theory

Up to now, the DFT has been considered in its generality and from a theoretical point of view. This part of the work focuses on the solid state theory and hence on concrete applications of the DFT to any system.

This section is mainly based on "MAPR2451: Atomistic and nanoscopic simulations" taught by Prof. G.-M. Rignanese [65].

3.3.1 The plane-wave basis set

A crystal can be seen as a periodic structure of repeated unit cells defined by three primitive translation vectors a_1, a_2 , and a_3 . The reciprocal space is defined by the vector $K = ua_1^* + va_2^* + wa_3^*$ where u, v , and w are integers and a_1^*, a_2^* and a_3^* are the primitive vectors of the reciprocal space defined by:

$$a_1^* = \frac{2\pi}{\Omega} (a_2 \times a_3) \quad a_2^* = \frac{2\pi}{\Omega} (a_3 \times a_1) \quad a_3^* = \frac{2\pi}{\Omega} (a_1 \times a_2) \quad (3.51)$$

with Ω the volume of the unit cell. The volume defined by the three primitive reciprocal vectors Ω^* is called the first Brillouin Zone (BZ).

For periodic systems, the electronic wave functions can be expressed as:

$$\phi_{nk}(r) = e^{ik \cdot r} u_{nk}(r) \quad (3.52)$$

thanks to the Bloch's theorem, where n and k label the band index and the wave vector of the wave function, respectively, and $u_{nk}(r)$ is a function with the periodicity R of the lattice, such that:

$$u_{nk}(r + R) = u_{nk}(r) \quad (3.53)$$

$$\phi_{nk}(r + R) = e^{ik \cdot R} \phi_{nk}(r) \quad (3.54)$$

The periodic part of the Bloch's function can be written as a Fourier series:

$$u_{nk}(r) = \sum_G u_{nk}(G) e^{iG \cdot r} \quad (3.55)$$

with the coefficients $u_{nk}(G)$ obtained by a Fourier transform:

$$u_{nk}(G) = \frac{1}{\Omega} \int_{\Omega} u_{nk}(r) e^{-iG \cdot r} dr \quad (3.56)$$

Thanks to the Born-von Karman boundary conditions, assuming N to be the number of unit cells repeated in the Born-von Karman periodic box and Ω to be the volume of the unperturbed unit cell, one can show that:

$$\phi_{nk}(r) = \frac{1}{\sqrt{N\Omega}} \sum_G e^{i(k+G) \cdot r} u_{nk}(G) \quad (3.57)$$

Coefficients $u_{nk}(K)$ for the lowest-energy eigenfunctions decrease exponentially with the kinetic energy $\frac{|k+G|^2}{2}$ [65]. From equation 3.57, one can see that a simple basis set to describe a periodic structure is composed of plane waves. For practical reasons, the plane waves to be considered in the sum are selected using a kinetic cut-off energy corresponding to a maximum allowed wave vector:

$$\frac{|k + G|^2}{2} < E_{\text{cut}} \quad (3.58)$$

The major problem is that a huge number of plane waves is required to properly describe strong oscillations of core orbitals and orbitals close to the nucleus (see figure 3.1).

3.3.2 Pseudopotentials

The idea is to use pseudopotentials to eliminate the small wavelength strong oscillations. Pseudopotentials are based on the idea that core electrons configurations are the same in

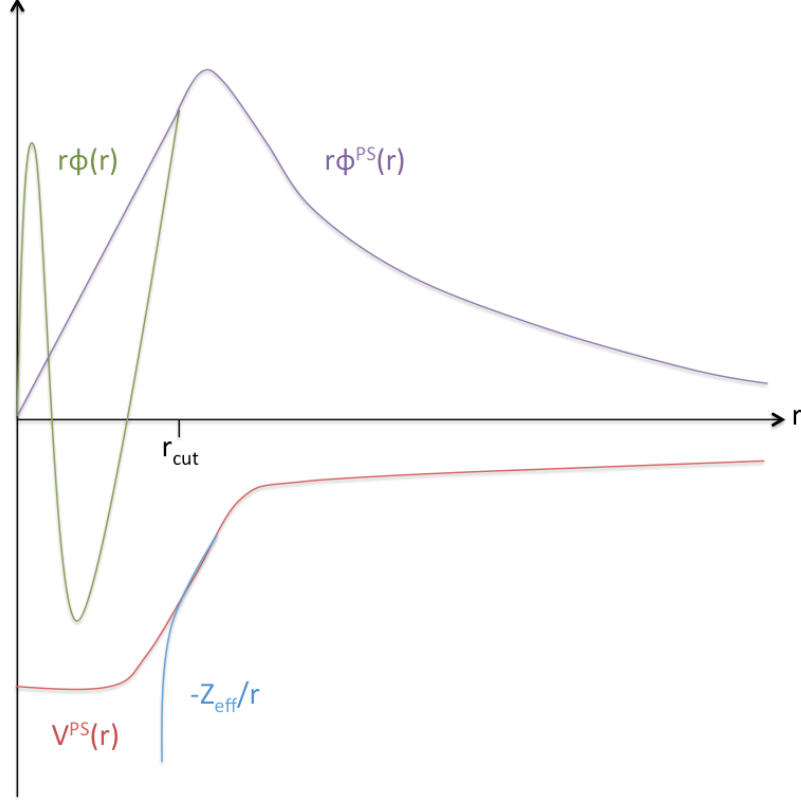


Figure 3.1: Schematic representation of the pseudopotential approximation. $\phi(r)$ (in green) corresponds to the all-electron wave function, $\phi^{\text{PS}}(r)$ (in purple) to the pseudo-wave function, V^{PS} (in red) to the pseudopotential and $-Z_{\text{eff}}/r$ (in blue) to the potential due to the ion with core electrons screening. Adapted from [5].

the atomic environment and in the bonding environment. The electronic density can thus be split into two components: a core term and a valence term:

$$\rho(r) = \sum_{i=1}^{N_e} \phi_i^*(r) \phi_i(r) = \sum_{i \in \text{core}}^{N_{e,\text{core}}} \phi_i^*(r) \phi_i(r) + \sum_{i \in \text{val}}^{N_{e,\text{val}}} \phi_i^*(r) \phi_i(r) \quad (3.59)$$

Core electrons are considered as frozen in their atomic configuration:

$$\phi_i(r) = \phi_i^{\text{atom}}(r) \quad (3.60)$$

As the distinction between core electrons and valence electrons is arbitrary, there exist numerous pseudopotentials with different efficiencies [5]. Pseudopotentials try to remove the strong changes within a cut-off radius $r < r_{\text{cut}}$. A pseudo-wave function ϕ^{PS} , which is a smooth wave function, is generated and properly matches the initial wave function for a radius higher than r_{cut} (see figure 3.1).

The pseudopotential approximation consists in solving the set of equations:

$$\left[-\frac{1}{2} \nabla^2 + V^{\text{PS}}(r) \right] \phi_i^{\text{PS}}(r) = \varepsilon_i^{\text{PS}} \phi_i^{\text{PS}}(r) \quad (3.61)$$

Various conditions can be imposed to pseudopotentials, such as the norm conservation, involving:

$$\varepsilon_i = \varepsilon_i^{\text{PS}} \quad (3.62)$$

$$\phi_i(r) = \phi_i^{\text{PS}}(r) \quad \text{for } r > r_{\text{cut}} \quad (3.63)$$

$$\int_0^{r_{\text{cut}}} |\phi_i(r)|^2 dr = \int_0^{r_{\text{cut}}} |\phi_i^{\text{PS}}(r)|^2 dr \quad (3.64)$$

Thanks to the pseudopotential approximation, it is possible to reduce the cut-off energy and hence the computation time.

3.3.3 Brillouin-zone integration

A last point concerns the Brillouin-zone integration for the calculation of functions of the wave function. For example, the electronic density:

$$\rho(r) = \sum_n \frac{1}{\Omega^*} \int_{\Omega^*} f(\varepsilon_F - \varepsilon_{nk}) \phi_{nk}^*(r) \phi_{nk}(r) dk \quad (3.65)$$

with $f(\varepsilon_F - \varepsilon_{nk})$ the Fermi-Dirac distribution function and ε_F the Fermi energy level, can be replaced, for practical reasons, by a weighted sum over a set of k-points:

$$\frac{1}{\Omega^*} \int_{\Omega^*} f_k dk \Rightarrow \sum_k w_k f_k \quad (3.66)$$

with $\sum_k w_k = 1$. There exist different choices for the sampling of the BZ. The one used in this work is the Monkhorst-Pack grid [87] which is a uniform grid. Then, the symmetry is taken into account to use the k-points in the Irreducible Brillouin Zone (IBZ) only with weights adapted as a function of the symmetry.

It is needed to do a convergence study with respect to both the kinetic cut-off energy E_{cut} and the sampling, as the accuracy of the results increases with E_{cut} and the number of k-points.

3.4 Density functional perturbation theory

Many physical properties can be derived from total energy variations with respect to external perturbations including small atomic displacements, characterized by a wave vector, that generate a basis for the description of phonons [88], and infinitesimal homogeneous electric fields. Related derivatives of the total energy such as dynamical matrices, dielectric permittivity tensors, and Born effective charge tensors can be obtained within the DFT using various methods [89–96].

For discrete values of perturbations, the simplest methods are referred to as direct approaches [89] and are based on finite differences calculations. For example, in the frozen phonon method, a small perturbation is frozen in the system and interatomic force constants [97] are computed. Afterwards, the perturbed system is compared to the corresponding unperturbed one. Another direct method consists in extracting phonon eigenfrequencies and eigenmodes from molecular dynamic trajectories [98]. These direct approaches present a series of limitations regarding the incommensurability with the periodic lattice or the decoupling of the responses to perturbation in different wavelengths. Moreover, commensurate perturbations can be handled through the use of supercells which increases the computation time.

By contrast to these direct approaches where perturbations are characterized by a wave vector, perturbative theories allow one to combine advantages of direct approaches without their drawbacks. The responses to perturbations are mapped onto an equivalent problem presenting the periodicity of the unperturbed system which suppress the problem of incommensurability [99]. Baroni, Giannozzi and Testa (BGT) [94–97, 99–101] have popularized

perturbative approaches in which the linear responses are calculated self-consistently [88]. The formalism proposed by Baroni et al. [94] is used with plane waves and pseudopotentials and has lead to numerous applications [102–104]. The BGT approach can easily be extended to nonlinear responses. Density Functional Perturbation Theory (DFPT) also allows to determine derivatives of the total energy and infers the existence of a variational principle for the second-order derivatives [96, 105] which can be used very efficiently for the first-order variations of wave functions, charge densities and self-consistent potentials [88]. The great advantage of DFPT in comparison to the BGT theory is the more rapid convergence of the self-consistent cycle. The efficiency of DFPT is also enhanced thanks to the used of Fast Fourier Transforms (FFT) and separable pseudopotentials.

This section is mainly based on *"First-principles responses of solids to atomic displacements and homogeneous electric field: Implementation of a conjugate-gradient algorithm"* by Xavier Gonze [88] and *"Dynamical matrices, Born effective charges, dielectric permittivity tensors, and interatomic force constants from density-functional perturbation theory"* by Xavier Gonze and Changyol Lee [106].

3.4.1 Basics of the perturbative theory

In DFT, one has defined the external potential V_{ext} . This one can be expressed as a Taylor series of the perturbation around a reference unperturbed external potential $V_{\text{ext}}^{(0)}$ in terms of a small parameter λ :

$$V_{\text{ext}}(\lambda) = V_{\text{ext}}^{(0)} + \lambda V_{\text{ext}}^{(1)} + \lambda^2 V_{\text{ext}}^{(2)} + \dots \quad (3.67)$$

All physical quantities will also be perturbed due to the change of the external potential such that they can also be developed into a Taylor series of the perturbation around the unperturbed solution $X^{(0)}$:

$$X(\lambda) = X^{(0)} + \lambda X^{(1)} + \lambda^2 X^{(2)} + \dots \quad (3.68)$$

where $X^{(k)}$ corresponds to (see appendix A for more details on the perturbation theory):

$$X^{(k)} = \frac{1}{k!} \frac{\partial^k X}{\partial \lambda^k} \quad (3.69)$$

and X can be the total energy E_{el} , the wave functions $\Psi(r)$, the electronic density $\rho(r)$, or the Hamiltonian operator $\hat{H}$. With the 1st order wave functions, both the 2nd and 3rd order perturbed energies can be obtained. It is possible to demonstrate that the n^{th} order wave functions give access to the $(2n)^{\text{th}}$ and $(2n+1)^{\text{th}}$ order energies [59]. This is called the $2n+1$ theorem [107].

3.4.2 Equations to be solved

There are different ways to get the 1st order wave functions in DFT. The first one is the minimization of the electronic energy functional:

$$E_{\text{el}}[\rho^{(0)}] = \sum_{i=1}^{N_e} \left\langle \Phi_i^{(0)} | T + V_{\text{ext}}^{(0)} | \Psi_i^{(0)} \right\rangle + E_{\text{Hxc}}^{(0)}[\rho^{(0)}] \quad (3.70)$$

where E_{Hxc} is the Hartree and exchange-correlation functional of density and $\rho^{(0)}$ is the ground-state electronic density given by:

$$\rho^{(0)}(r) = \sum_{i=1}^{N_e} \left[\Psi_i^{(0)}(r) \right]^* \Psi_i^{(0)}(r) \quad (3.71)$$

and under the constraint:

$$\langle \Psi_i^{(0)} | \Psi_j^{(0)} \rangle = \delta_{ij} \quad (3.72)$$

A second way involves the self-consistent resolution of the reference Schrödinger equations (the Kohn Sham equations):

$$H^{(0)} \Psi_i^{(0)} = \left[-\frac{1}{2} \nabla^2 + V_{\text{ext}}^{(0)} + V_{\text{Hxc}}^{(0)} \right] \Psi_i^{(0)} = \varepsilon_i^{(0)} \Psi_i^{(0)} \quad (3.73)$$

where the Hartree and exchange-correlation potential is given by:

$$V_{\text{Hxc}}^{(0)}(r) = \frac{\delta E_{\text{Hxc}}[\rho^{(0)}]}{\delta \rho(r)} \quad (3.74)$$

When including the DFPT formalism and considering a perturbed system, equation 3.70 becomes:

$$E_{\text{el}}[\rho(\lambda)] = \sum_{i=1}^{N_e} \langle \Psi_i(\lambda) | T + V_{\text{ext}}(\lambda) | \Psi_i(\lambda) \rangle + E_{\text{Hxc}}[\rho(\lambda)] \quad (3.75)$$

with the electronic density:

$$\rho(r, \lambda) = \sum_{i=1}^{N_e} \Psi_i^*(r, \lambda) \Psi_i(r, \lambda) \quad (3.76)$$

and under the constraint:

$$\langle \Psi_i(\lambda) | \Psi_j(\lambda) \rangle = \delta_{ij} \quad (3.77)$$

For the second way, equation 3.73 becomes:

$$H(\lambda) \Psi_i(\lambda) = \left[-\frac{1}{2} \nabla^2 + V_{\text{ext}}(\lambda) + V_{\text{Hxc}}(\lambda) \right] \Psi_i(\lambda) = \varepsilon_i(\lambda) \Psi_i(\lambda) \quad (3.78)$$

where the Hartree and exchange-correlation potential is given by:

$$V_{\text{Hxc}}(r, \lambda) = \frac{\delta E_{\text{Hxc}}[\rho(\lambda)]}{\delta \rho(r)} \quad (3.79)$$

Thanks to the perturbation theory (see appendix A), it is equivalent to solve self-consistently the Sternheimer equations [59] with:

$$\left(\hat{H}^{(0)} - \varepsilon_i^{(0)} \right) \Psi_i^{(1)} = - \left(\hat{H}^{(1)} - \varepsilon_i^{(1)} \right) \Psi_i^{(0)} \quad (3.80)$$

$$\hat{H}^{(1)} = \left(\hat{T} + V_{\text{ext}} \right)^{(1)} + \int \frac{\delta^2 E_{\text{Hxc}}}{\delta \rho(r) \delta \rho(r')} \rho^{(1)}(r') dr' \quad (3.81)$$

$$\varepsilon_i^{(1)} = \langle \Psi_i^{(0)} | \hat{H}^{(1)} | \Psi_i^{(0)} \rangle \quad (3.82)$$

3.4.3 Atomic displacement and homogeneous electric field

Let us consider an unperturbed periodic system with:

$$V_{\text{ext}}^{(0)}(r + R_a) = V_{\text{ext}}^{(0)}(r) \quad (3.83)$$

For a perturbation characterized by a wave vector q :

$$V_{\text{ext}}^{(1)}(r + R_a) = e^{iq \cdot R_a} V_{\text{ext}}^{(1)}(r) \quad (3.84)$$

it can be shown that all the responses, at linear order, will be characterized by the same wave vector q :

$$\Psi_{i,k,q}^{(1)}(r + R_a) = e^{iq \cdot R_a} \Psi_{i,k,q}^{(1)}(r) \quad (3.85)$$

$$\rho^{(1)}(r + R_a) = e^{iq \cdot R_a} \rho^{(1)}(r) \quad (3.86)$$

The related periodic quantities are defined as:

$$u_{i,k,q}^{(1)}(r) = \sqrt{N\Omega_0} e^{-i(k+q) \cdot r} \Psi_{i,k,q}^{(1)}(r) \quad (3.87)$$

$$\bar{\rho}^{(1)}(r) = e^{-iq \cdot r} \rho^{(1)}(r) \quad (3.88)$$

Equations of DFPT only involve these periodic quantities such that the phases $e^{-iq \cdot r}$ and $e^{-i(k+q) \cdot r}$ can be factorized [59, 108]. It highlights the great advantage of DFPT where perturbations incommensurate with the unperturbed system periodicity are mapped onto this unperturbed periodic system. It will be shown in section 3.4.3 that it is particularly interesting for electric fields treatment.

Dynamical matrix and phonon frequencies

Phonons correspond to collective vibrations of a periodic arrangement of atoms or molecules and play a major role especially in thermal and electrical conductivities. Thanks to DFPT, it is possible to determine their frequencies and displacement patterns. Based on the harmonic approximation, the total energy of a periodic system with small lattice distortion from its equilibrium position is given by the following quadratic expression [106]:

$$E_{\text{tot}}(u_{\kappa\alpha}^a, u_{\kappa'\alpha'}^{a'}) = E_{\text{tot}}^{(0)} + \frac{1}{2} \sum_{a\kappa\alpha} \sum_{a'\kappa'\alpha'} \left(\frac{\partial^2 E_{\text{tot}}}{\partial R_{\kappa\alpha}^a \partial R_{\kappa'\alpha'}^{a'}} \right) u_{\kappa\alpha}^a(t) u_{\kappa'\alpha'}^{a'}(t) \quad (3.89)$$

where α and α' refer to cartesian directions, and $u_{\kappa\alpha}^a$ is the displacement along direction α of the atom κ in the cell a . The matrix of interatomic force constants (IFCs) is defined as:

$$C_{\kappa\alpha, \kappa'\alpha'}(a, a') = \frac{\partial^2 E_{\text{tot}}}{\partial R_{\kappa\alpha}^a \partial R_{\kappa'\alpha'}^{a'}} \quad (3.90)$$

Thanks to the translational invariance, its Fourier transform:

$$\begin{aligned} \tilde{C}_{\kappa\alpha, \kappa'\alpha'}(q) &= \frac{1}{N} \sum_{a, a'} C_{\kappa\alpha, \kappa'\alpha'}(a, a') e^{-iq \cdot (R_a - R_{a'})} \\ &= \sum_{a'} C_{\kappa\alpha, \kappa'\alpha'}(0, a') e^{iq \cdot R_{a'}} \end{aligned} \quad (3.91)$$

allows to determine frequencies and eigenvectors as solutions of the following eigenvalues problem:

$$\sum_{\kappa'\alpha'} \tilde{C}_{\kappa\alpha, \kappa'\alpha'}(q) U_{mq}(\kappa'\alpha') = M_{\kappa} \omega_{mq}^2 U_{mq}(\kappa\alpha) \quad (3.92)$$

where ω_{mq} 's are the phonon frequencies, $U_{mq}(\kappa\alpha)$'s correspond to the phonon displacement patterns, m is an index referencing the phonon mode and q is a vector from the reciprocal space.

The IFC's matrix is connected to the dynamical matrix $\tilde{D}_{\kappa\alpha, \kappa'\alpha'}(q)$ by:

$$\tilde{D}_{\kappa\alpha, \kappa'\alpha'}(q) = \frac{\tilde{C}_{\kappa\alpha, \kappa'\alpha'}}{\sqrt{M_{\kappa} M_{\kappa'}}} \quad (3.93)$$

Equation 3.92 can be rewritten as:

$$\sum_{\kappa'\alpha'} \tilde{D}_{\kappa\alpha,\kappa'\alpha'}(q) U_{mq}(\kappa'\alpha') = \omega_{mq}^2 U_{mq}(\kappa\alpha) \quad (3.94)$$

This equation gives rise to 3 acoustic modes and $3N_{\text{at}}-3$ optical modes as a function of q with N_{at} the number of atoms in the unit cell.

When the dynamical matrices are known for a sufficiently fine grid of wave vectors, it is possible to generate the IFC's matrix and to calculate the phonon eigenfrequencies for each wave vector in the Brillouin zone using a Fourier transformation [106].

Electronic dielectric permittivity tensor

The dielectric permittivity tensor can be seen as the coefficient of proportionality between the macroscopic displacement field $\mathcal{D}_{\text{mac},\alpha}$ and the external macroscopic electric field $\mathcal{E}_{\text{mac},\alpha}$, in the linear regime:

$$\mathcal{D}_{\text{mac},\alpha} = \sum_{\alpha'} \epsilon_{\alpha\alpha'} \mathcal{E}_{\text{mac},\alpha'} \quad (3.95)$$

When a material undergoes an external macroscopic electric field $\mathcal{E}_{\text{mac},\alpha}$, its polarization per unit cell is modified following the Taylor series expression of the electric field [109]:

$$\mathcal{P}_{\text{mac},\alpha} = \mathcal{P}_{\text{mac},\alpha}^S + \sum_{\alpha'} \chi_{\alpha\alpha'}^{(1)} \mathcal{E}_{\text{mac},\alpha'} + \sum_{\alpha'\alpha''} \chi_{\alpha\alpha'\alpha''}^{(2)} \mathcal{E}_{\text{mac},\alpha'} \mathcal{E}_{\text{mac},\alpha''} + \dots \quad (3.96)$$

where $\mathcal{P}_{\text{mac},\alpha}^S$ is the spontaneous polarization of the system, $\chi_{\alpha\alpha'}^{(1)}$ the linear dielectric susceptibility and $\chi_{\alpha\alpha'\alpha''}^{(2)}$ the second-order nonlinear susceptibility.

The dielectric permittivity can be defined as [92, 110]:

$$\epsilon_{\alpha\alpha'} = \frac{\partial \mathcal{D}_{\text{mac},\alpha}}{\partial \mathcal{E}_{\text{mac},\alpha'}} = \delta_{\alpha\alpha'} + 4\pi \frac{\partial \mathcal{P}_{\text{mac},\alpha}}{\partial \mathcal{E}_{\text{mac},\alpha'}} \quad (3.97)$$

In general, for low-frequency electric field, the dielectric permittivity includes a contribution from the electronic polarization called the optical dielectric permittivity $\epsilon_{\alpha\alpha'}^\infty$, linked to the mixed second-order derivative of the energy with respect to the electric field. It also includes contributions from ionic displacements which will be treated later.

When the perturbation is a homogeneous electric field, the first-order perturbed external potential is expressed by [88]:

$$V_{\text{ext}}^{(1)} = \mathcal{E} \cdot r \quad (3.98)$$

and breaks the periodicity of the crystal lattice as its intensity increases linearly with the space (r). It can be demonstrated that this problem can be overcome by solving the Sternheimer equation involving the Bloch functions [88]:

$$P_{C,k} [r|u_{v,k}\rangle] = P_{C,k} [-i\nabla_k|u_{v,k}\rangle] \quad (3.99)$$

where P_C is the projector on the conduction states.

Born effective charges and sum rules

The Born effective charge tensor $Z_{\kappa\alpha\alpha'}^*$ describes the coupling between a collective atomic displacement and a homogeneous electric field. The perturbed system undergoes a modification of its macroscopic polarization and the Born effective charge $Z_{\kappa\alpha\alpha'}^*$ is defined as the proportionality coefficient, at linear order, between the macroscopic polarization per unit

cell in the direction α and the displacement in the direction α' of atoms belonging to the sublattice κ [106]:

$$Z_{\kappa\alpha\alpha'}^* = \Omega_0 \left. \frac{\partial \mathcal{P}_{\text{mac},\alpha}}{\partial u_{\kappa\alpha'}(q=0)} \right|_{\mathcal{E}_{\text{mac},\alpha}=0} = \left. \frac{\partial F_{\kappa\alpha'}}{\partial \mathcal{E}_{\text{mac},\alpha}} \right|_{u_{\kappa\alpha'}=0} \quad (3.100)$$

As mentionned in equation 3.100, the Born effective charge tensor also describes the linear relation between the force in the direction α' and the macroscopic electric field. Both approaches can be connected to the mixed second-order derivative of the energy with respect to a macroscopic electric field and to atomic displacements. In order to evaluate the accuracy of the obtained results, convergence studies are performed with respect to numerous numerical parameters, including the number of plane waves (fixed by the kinetic cut-off energy), and the sampling of the Brillouin zone (determined by the k-point grid).

A few sum rules are available in order to monitor these convergence studies. Among them, the acoustic sum rule [111] is based on the invariance of the total energy (and the force on one atom) with respect to any translation and states that the dynamical matrix at the Gamma point ($q = 0$) should admit the homogeneous translation of the crystal as an eigenvector with a zero frequency [106]:

$$\begin{aligned} 0 &= \sum_{\kappa'\alpha'} \frac{\partial F_{\kappa,\alpha}}{\partial r_{\kappa',\alpha'}} \cdot u_{\alpha'} = \sum_{\kappa'\alpha'} \tilde{C}_{\kappa\alpha,\kappa'\alpha'}(q=0) \cdot u_{\alpha'} \\ &\Leftrightarrow \sum_{\kappa'} \tilde{C}_{\kappa\alpha,\kappa'\alpha'}(q=0) = 0 \end{aligned} \quad (3.101)$$

The second sum rule is based on the polarization invariance and guarantees the charge neutrality of the system at the level of the Born effective charges such that [112]:

$$\begin{aligned} 0 &= \sum_{\kappa\alpha'} \frac{\partial \mathcal{P}_\alpha}{\partial r_{\kappa,\alpha'}} \cdot u_{\alpha'} = \sum_{\kappa\alpha'} Z_{\kappa\alpha\alpha'}^* \cdot u_{\alpha'} \\ &\sum_{\kappa} Z_{\kappa\alpha\alpha'}^* = 0 \end{aligned} \quad (3.102)$$

Low-frequency dielectric permittivity

As previously mentioned, the macroscopic low-frequency dielectric permittivity tensor $\epsilon_{\alpha\alpha'}(\omega)$ including a contribution from the electronic polarization referred to as the optical dielectric permittivity $\epsilon_{\alpha\alpha'}^\infty$, also has to take the response of ions into account. Indeed, the force involved by the macroscopic electric field modifies the motion of the ions which, in turn, creates a polarization. Maradudin et al. [113] proposed to add the ionic contribution to $\epsilon_{\alpha\alpha'}^\infty$ in the following way:

$$\epsilon_{\alpha\alpha'}(\omega) = \epsilon_{\alpha\alpha'}^\infty + \frac{4\pi}{\Omega_0} \sum_m \frac{S_{m,\alpha\alpha'}}{\omega_m^2 - \omega^2} \quad (3.103)$$

with $S_{m,\alpha\alpha'}$, the mode-oscillator strength tensor defined as:

$$S_{m,\alpha\alpha'} = \left(\sum_{\kappa\beta} Z_{\kappa\alpha\beta}^* U_{m,q=0}^*(\kappa\beta) \right) \left(\sum_{\kappa'\beta'} Z_{\kappa'\alpha'\beta'} U_{m,q=0}(\kappa'\beta') \right) \quad (3.104)$$

LO-TO splitting

For a system constituted of N_{at} atoms in the unit cell, there are $3N_{\text{at}}-3$ optical modes and 3 acoustic modes. Optical modes can be either longitudinal (LO) or transverse (TO) depending on the atomic displacement with respect to q . When there is no electric field, both longitudinal and transverse modes are degenerated while the motion of an ion with charge Z from its equilibrium position involves the creation of a dipolar electric field and the degeneracy is lifted. It is possible to demonstrate that this dipolar electric field at $q = 0$ can be treated separately [88, 112]:

$$\tilde{C}_{\kappa\alpha,\kappa'\alpha'}(q \rightarrow 0) = \tilde{C}_{\kappa\alpha,\kappa'\alpha'}(q = 0) + \tilde{C}_{\kappa\alpha,\kappa'\alpha'}^{\text{NA}}(q \rightarrow 0) \quad (3.105)$$

where the nonanalytical, direction-dependent, term is given by:

$$\tilde{C}_{\kappa\alpha,\kappa'\alpha'}^{\text{NA}}(q \rightarrow 0) = \frac{4\pi}{\Omega} \frac{\left(\sum_{\beta} q_{\beta} Z_{\kappa\beta\alpha}^*\right) \left(\sum_{\beta'} q_{\beta'} Z_{\kappa'\beta'\alpha'}^*\right)}{\sum_{\beta\beta'} q_{\beta} \epsilon_{\beta\beta'}^{\infty} q_{\beta'}} \quad (3.106)$$

Transverse modes to the direction of q are common for $\tilde{C}(q \rightarrow 0)$ matrix and $\tilde{C}(q = 0)$ matrix, while it is not the case for longitudinal modes. In fact, the nonanalytical term acts in a space perpendicular to the one spanned by the TO modes.

When symmetry constraints are sufficient to guarantee that some modes of $\tilde{C}(q \rightarrow 0)$ and of $\tilde{C}(q = 0)$ are identical, LO frequencies for $q \rightarrow 0$ are related to TO frequencies by [106]:

$$\omega_m^2(q \rightarrow 0) = \omega_m^2(q = 0) + \frac{4\pi}{\Omega} \frac{\sum_{\alpha\alpha'} q_{\alpha} S_{m,\alpha\alpha'} q_{\alpha'}}{\sum_{\alpha\alpha'} q_{\alpha} \epsilon_{\alpha\alpha'}^{\infty} q_{\alpha'}} \quad (3.107)$$

In summary, the longitudinal optic (LO) - transverse optic (TO) splitting of phonon modes and the directionality-dependence of the Gamma limit originate from the long-wave-vector electric field caused by the polarization involved by the atomic displacements.

3.5 Spin-orbit coupling

Up to now, we have not considered the spin of the electron and its influence on the total electronic energy. However, by the mean of the spin-orbit coupling, it is clear that the Hamiltonian of the system depends on the global spin configuration. Instead of only their position, electrons have to be characterized by both their position r and their spin $\sigma = \uparrow$ or $\downarrow$. The Hamiltonian of equation 3.5 is modified in the following way [114]:

$$\hat{H}_{\{R\}}^e = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} + \hat{H}_{\text{SO}} = \hat{H}_{\text{KS}} + \hat{H}_{\text{SO}} \quad (3.108)$$

with:

$$\hat{H}_{\text{SO}} = \sum_i \chi(r_i) L_i \cdot S_i \quad (3.109)$$

the spin-orbit contribution to the total energy. $\chi(r_i)$ is related to the derivative of the potential of the electron i , while L_i and S_i are the orbital and spin angular momenta, respectively.

In order to take the spin of the electron into account, the electronic density has to be of the form of a 2x2 matrix:

$$n^{\alpha\beta}(r) = \sum_{\sigma_2, \sigma_{N_e}} \int \Psi^*(r, \sigma_{\alpha}, r_2, \sigma_2, \dots, r_{N_e}, \sigma_{N_e}) \Psi(r, \sigma_{\beta}, r_2, \sigma_2, \dots, r_{N_e}, \sigma_{N_e}) dr_2 \dots dr_{N_e} \quad (3.110)$$

Even when no magnetic field is applied, the ground-state may be spin-polarized, which means that a spin-degenerate level can be split by spin-orbit coupling into levels with spin parallel and antiparallel to the orbit.

As the power of the approximations to the exchange-correlation functional of the DFT has been proved, it is interesting to derive an expression for the global Hamiltonian on which the Hohenberg and Kohn theorem can be applied. To do so, the approximation that the spin-orbit coupling contribution only acts on the spin and does not affect the orbital motion is required. A consequence of this assumption is that the spin-orbit coupling contribution to the energy can be neglected. In this case, the electronic density becomes a diagonal matrix:

$$n^{\alpha\beta}(r) = \begin{pmatrix} n^{11}(r) & 0 \\ 0 & n^{22}(r) \end{pmatrix} \quad (3.111)$$

with $n^{11}(r) = n^\uparrow(r)$ for spin up and $n^{22}(r) = n^\downarrow(r)$ for spin down.

Based on that, the total electronic density is defined as:

$$n(r) = n^\uparrow(r) + n^\downarrow(r) \quad (3.112)$$

and the spin density as:

$$s(r) = n^\uparrow(r) - n^\downarrow(r) \quad (3.113)$$

The energy functional can be rewritten as a function of the total electronic density [5]:

$$E^{\text{el}}[n] = T_s[n] + V_H[n] + \int V_{\text{ext}}(r)n(r)dr + E_{\text{xc}}[n, s] \quad (3.114)$$

If we assume that the exchange-correlation functional can be separated for each spin population such that $E_{\text{xc}}[n, s] \rightarrow E_{\text{xc}}[n^\uparrow, n^\downarrow]$, equation 3.114 can be simplified and the solution of the spin-dependent many-body problem is given by the resolution of two equations (one for each spin) [5] of the form:

$$\left[-\frac{\nabla^2}{2} + V_{\text{KS}}^\sigma(r) \right] \Psi_i^\sigma(r) = \varepsilon_i^\sigma \Psi_i^\sigma(r) \quad (3.115)$$

where

$$V_{\text{KS}}^\sigma(r) = V_{\text{ext}}(r) + \int \frac{n(r')}{|r - r'|} dr' + V_{\text{xc}}^\sigma(r) \quad (3.116)$$

is the effective Kohn and Sham potential for spin σ . Only the exchange-correlation potential is spin-dependent and it is given by:

$$V_{\text{xc}}^\sigma(r) = \frac{\partial E_{\text{xc}}[n^\uparrow, n^\downarrow]}{\partial n^\sigma(r)} \quad (3.117)$$

The exchange-correlation functional $E_{\text{xc}}[n^\uparrow, n^\downarrow]$ contains the interaction between spin $\uparrow$ and spin $\downarrow$.

In this framework, the electronic density for each spin σ can be determined thanks to the following expression:

$$n^\sigma(r) = \sum_i^{\text{occ}} \Psi_i^{\sigma*}(r) \Psi_i^\sigma(r) \quad (3.118)$$

Several approximations to the exchange-correlation functional have been adapted in order to take the spin-orbit effects into account.

Chapter 4

Ab initio results

4.1 Structural and electronic properties

The main aim of this section is the study of the structural and electronic properties of the orthorhombic polymorph of $\text{CH}_3\text{NH}_3\text{PbI}_3$. Different parameters are computed such as the lattice parameters, the interatomic distances, the total energy and the electronic band structure.

All these parameters are first computed without considering any physico-chemical effect. Afterwards, van der Waals corrections and relativistic spin-orbit effects are taken into account in order to get a more physical representation of the crystal.

4.1.1 Computational parametrization

As introduced in the previous chapter, it is necessary, for all properties under study, to converge the results with respect to the kinetic energy cut-off and the density of the Monkhorst grid. In this work, *ab initio* calculations are performed in the framework of the density functional theory (DFT), based on plane-wave basis set for the expansion of the single-particle Kohn-Sham wave functions and pseudopotentials. ONCVSP-PBE scalar-relativistic norm-conserving pseudopotentials are used and the Perdew-Burke-Ernzerhof (PBE) parametrization of the Generalized Gradient Approximation (GGA) [66] is employed for the evaluation of the exchange-correlation energy. The following valence atomic configurations are considered: Pb:5d¹⁰6s²6p² (with semicore states) and I:5s²5p² (without semicore states).

The convergence criteria for the structural properties have been set to 0.5 mHa/atom for the total energy and 0.2% of relative difference with respect to an asymptotic value for the relaxed lattice parameters. As there are 48 atoms in the orthorhombic cell of $\text{CH}_3\text{NH}_3\text{PbI}_3$, the tolerance on the energy is 24 mHa. The electronic wave functions have been expanded using plane waves corresponding to energies up to 30 Hartree and a 3x2x3 Monkhorst-pack grid [87] has been chosen for sampling the Brillouin zone of the orthorhombic cell in the direct lattice in order to satisfy the convergence criteria.

The spin-orbit coupling has been introduced by using fully-relativistic pseudopotentials as implemented in the ABINIT software.

DFT-D methods have been implemented in the ABINIT software [17, 18] for ground state calculations including van der Waals corrections. The GGA-PBE approximation is adopted for the exchange-correlation functional in addition to the DFT-D methods [71]. As it is not possible to compute the contributions to the energy, forces, and stresses for an infinite number of cell replica, a tolerance parameter defining the number of cells to be considered is used in the DFT-D correction. The cut-off radius introduced in section 3.2.3 is set to 200 Bohr and a tolerance of 10¹² Ha is used on the energy for the pair-wise term. An energy

cut-off smearing [115] of 1.0d-4 Ha is used and the stopping criterion on the residual of the forces on each atom is set to 5.0d-5 Ha/Bohr, for the geometry optimizations. As already mentioned in 3.2.3, the three-body contribution is neglected.

All the calculations have been done using the ABINIT software [17, 18].

4.1.2 Structural properties

The normal modes of a system are defined for an equilibrium configuration. Evaluating the vibrations apart from the equilibrium structure will result in imaginary frequencies upon diagonalizing the dynamical matrix [50]. Therefore, lattice parameters must be released numerically. This is done by allowing the atoms to move in a way that minimizes the forces present in the cell. The relaxation of the structure allows the determination of the atomic positions at the equilibrium. The parameter `ionmov` is used in order to conduct structural optimization using the Broyden-Fletcher-Goldfarb-Shanno minimization (BFGS) to take into account the total energy as well as the gradients.

For the lattice parameters, our results as well as values found in the literature are given in table 4.1.

XCF	PBE	PBEsol [11]	PND (100 K) [11]	X-ray [12]
ecut [Ha]	30	25		
ngkpt	3x2x3	5x4x5		
a [Å]	8.58	8.35	8.58	8.56
b [Å]	12.91	12.66	12.63	12.58
c [Å]	9.34	9.04	8.87	8.84

Table 4.1: Computed lattice parameters calculated with the Perdew-Burke-Ernzerhof (PBE) parametrization (this work) and PBEsol [11], as well as experimental data from Refs. [11] and [12].

Our results are in good agreement with experimental results. The relative error with respect to the experimental value on the lattice constants does not exceed 5%. As expected from the approximation of the exchange-correlation functional, GGA overestimates the lattice parameters [5].

The lattice parameters are studied for different parametrizations: PBE, DFT-D3, DFT-D3(BJ), PBE+SOC, DFT-D3+SOC, and DFT-D3(BJ) referring respectively to normal ground-state calculations with the PBE exchange-correlation functional (XCF), the PBE XFC in addition to the DFT-D3 method, the PBE XFC in addition to the DFT-D3(BJ) method, the PBE XFC including fully-relativistic spin-orbit effects, the PBE XFC in addition to the DFT-D3 method including fully-relativistic spin-orbit effects, and the PBE XFC in addition to the DFT-D3(BJ) method including fully-relativistic spin-orbit effects. Results are summarized in table 4.2.

Based on these results, it is possible to see that the inclusion of van der Waals corrections leads to an estimation of the lattice parameters which is more closed to the experimental data reported in Refs. [11] and [12]. However, columns 4, 5, and 6 of table 4.2 are almost similar to columns 1, 2, and 3 respectively, highlighting the fact that spin-orbit effects only have a small influence on the structural properties.

Besides the lattice parameters, the reduced coordinates of each atom are also modified due to the relaxation. The orthorhombic symmetry is still conserved. The total energy of the

XCF	PBE	DFT-D3	DFT-D3(BJ)	PBE +SOC	DFT-D3 +SOC	DFT-D3(BJ) +SOC
ecut [Ha]	30	30	30	30	30	30
ngkpt	3x2x3	3x2x3	3x2x3	3x2x3	3x2x3	3x2x3
<i>a</i> [Å]	8.58	8.41	8.38	8.60	8.41	8.39
<i>b</i> [Å]	12.91	12.75	12.72	12.91	12.74	12.70
<i>c</i> [Å]	9.34	9.01	9.05	9.36	9.02	9.06
Vol [Å ³]	1034.57	966.12	964.67	1039.20	966.43	965.37
Energy [Ha]	-515.07	-515.27	-515.29	-516.42	-516.62	-516.63

Table 4.2: Computed lattice parameters and cell volume calculated with the Perdew-Burke-Ernzerhof (PBE) parametrization (1st column) compared to the ones calculated when including the van der Waals interactions (2nd and 3rd columns), the relativistic effects (4th column) and both effects (5th and 6th columns). Ground-state energies are also mentioned.

relaxed system is found to be equal to -515.07 Hartree. This ground-state energy decreases when including the physical effects, as shown in table 4.2.

These assumptions can be visualized in figure 4.1 showing the polyhedral model of the optimized orthorhombic structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ for the different parametrizations.

Figures 4.1(a) and 4.1(d) are almost identical, meaning that the spin-orbit coupling does not affect neither the lattice parameters nor the bond angles, while van der Waals interactions induce several changes in the configuration of the perovskite crystal. First of all, the system is tilted to the right along the *b* axis. Besides, the distance between the organic (CH_3NH_3) and inorganic (PbI_3) compounds decreases when including the van der Waals interactions, as it could be expected thanks to the physical meaning of van der Waals forces. These modifications are much more pronounced for the DFT-D3 study (figure 4.1(b)) than for the DFT-D3(BJ) one (figure 4.1(c)).

In addition to the study of the lattice parameters, it's interesting to have a look at the interatomic distances and the internal bond angles. The optimized Pb-I bond length calculated with PBE is 3.27 Å while the C-H, N-H and C-N bond lengths are 1.09, 1.04, and 1.49 Å, respectively. These values are in good agreement with the experimental values of 3.18, 1.1, 1.0, and 1.57 Å. The Pb-I bond length becomes still more closed to the experimental value when including the van der Waals interactions. Spin-orbit coupling again does not affect these interatomic distances. In the case of the organic-inorganic distance, it is shown to decrease when either the DFT-D3 or the DFT-D3(BJ) method is used. The apical (along the *b* axis) and equatorial (along the *c* axis) Pb-I-Pb angles are respectively equal to 167.83° and 150.88° and compare well with the experimental values of 161.9° and 150.7°. While the apical angle compare better with the experimental value when including the van der Waals interactions, it is not the case for the equatorial angle which is better estimated with the PBE exchange-correlation functional. All the results concerning the interatomic distances and the internal bond angles are summarized in table 4.3.

In the next sections, the electronic and vibrational properties are calculated using optimized lattice parameters from table 4.2. These parameters are all within 5% from the corresponding experimental values [12].

4.1.3 Electronic band structure

Representing the band structure for the 3D grid of the Brillouin zone is impossible as it requires a four-dimensional plot. A more convenient way to represent it consists in defining paths along high symmetric directions. The study of the band structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is

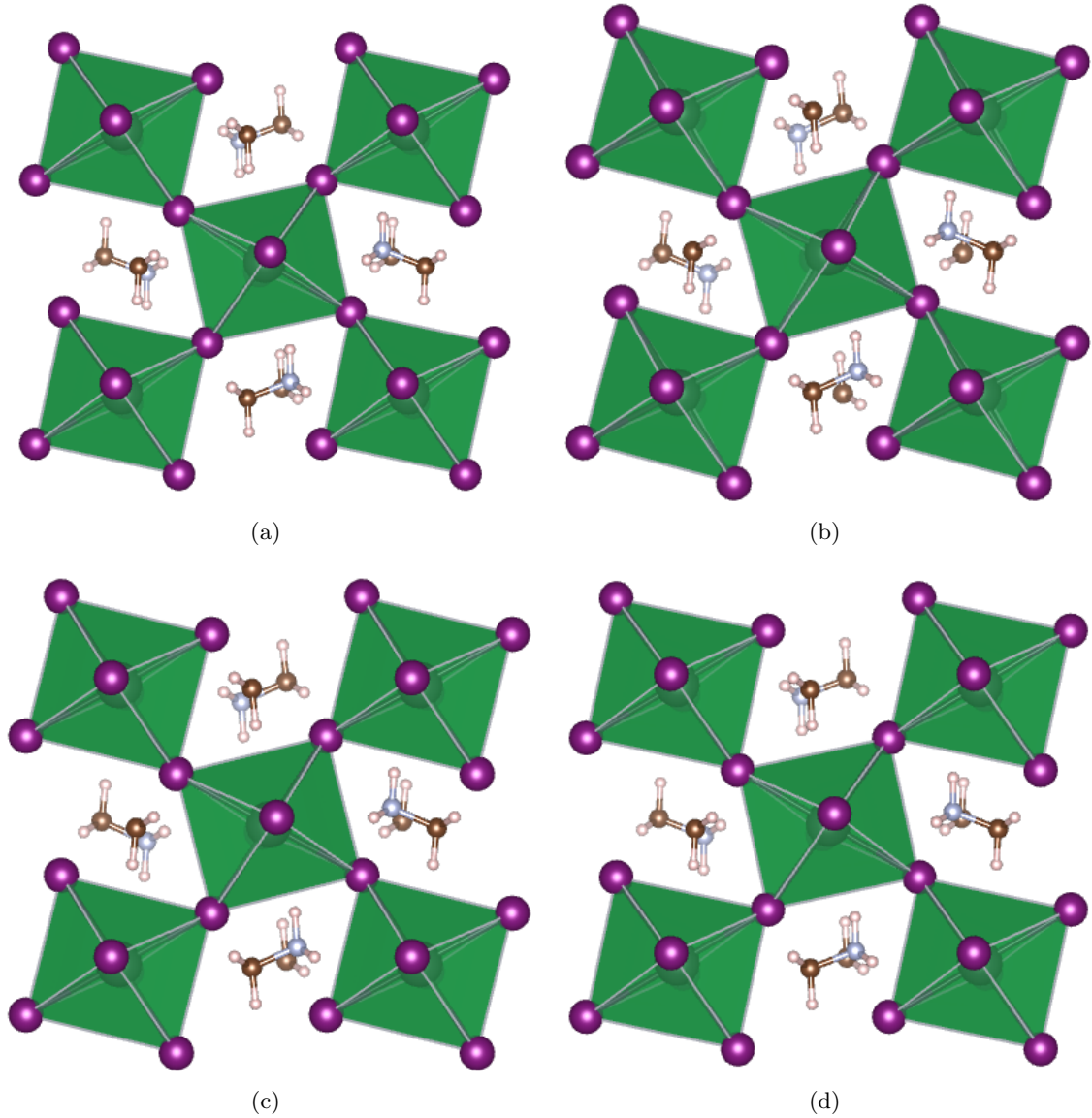


Figure 4.1: Polyhedral model of the optimized orthorhombic structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$, with the Pb atoms (grey spheres) located at the center of the octahedra and the I atoms (purple spheres) at the corners. The octahedra are connected in a corner-sharing configuration. The MA cations are located inside the cuboctahedral cages defined by the Pb and I atoms. Depending on the parametrization, the structural parameters are changing. The exchange-correlation functionals and methods used are respectively: (a) PBE, (b) DFT-D3, (c) DFT-D3(BJ) and (d) PBE+SOC. They are all seen along the b axis.

interesting as it gives information about the electronic transition.

The acquisition of a band structure is a two-step process. Firstly, the density must be obtained thanks to a self-consistent calculation. Secondly, the density is used when solving the Kohn-Sham equation for many different k points, along the defined paths in the Brillouin zone. It ensures that the potential will not vary during the scan of different k points lines. The Brillouin zone of the orthorhombic cell is represented in figure 4.2.

Bond [Å]/ angle [°]	PBE	DFT-D3	DFT-D3(BJ)	PBE +SOC	DFT-D3 +SOC	DFT-D3(BJ) +SOC	EXP [12]
Pb-I	3.27	3.22	3.21	3.27	3.22	3.19	3.18
Pb-C	5.23	5.16	5.11	5.23	5.16	5.12	
C-H	1.09	1.09	1.09	1.09	1.09	1.09	1.10
N-H	1.04	1.04	1.04	1.04	1.04	1.04	1.00
C-N	1.49	1.49	1.49	1.49	1.49	1.49	1.57
Pb-I-Pb	167.83	166.51	167.14	167.83	166.64	167.21	161.9
apical							
Pb-I-Pb	150.88	146.26	148.52	150.88	146.41	148.94	150.7
equatorial							

Table 4.3: Computed bond lengths and angles calculated with the PBE parametrization (1st column) compared to the ones calculated when including the van der Waals interactions (2nd and 3rd columns), the relativistic effects (4th column) and both effects (5th and 6th columns). The 6th column includes experimental results reported by Baikie et al. [12].

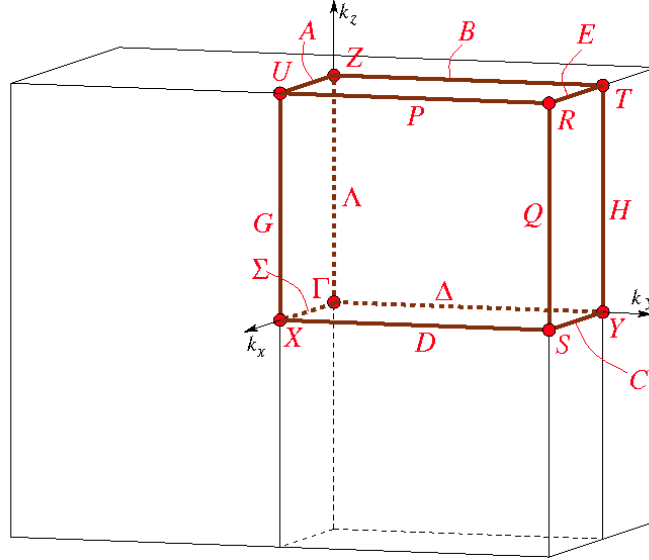


Figure 4.2: Brillouin zone of space group $Pnma$ [6].

Let's consider the following directions of high symmetry:

$$X(0.5, 0, 0); \Gamma(0, 0, 0); Z(0, 0, 0.5); U(0.5, 0, 0.5); X; S(0.5, 0.5, 0); Y(0, 0.5, 0); \Gamma \quad (4.1)$$

The band structure (depicted at the converged parameters) is represented in figure 4.3. Red lines are conduction bands while blue ones are valence bands. It is possible to see that the orthorhombic phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$ exhibits a direct band gap occurring at the Γ point (0,0,0) which is the highest symmetrical point of the Brillouin zone. The band gap is almost equal to ~ 1.81 eV.

Band structures calculated with the DFT-D3 and DFT-D3(BJ) methods are depicted in figures 4.4(a) and 4.4(b) respectively. The band gap values obtained with the different approximations are summarized in table 4.4.

In general, when using LDA or GGA calculation methods, the band gap is often underestimated, it is the famous DFT band-gap problem. In the case of $\text{CH}_3\text{NH}_3\text{PbI}_3$, the band gap calculated within scalar-relativistic DFT is in apparent agreement with experiment. This effect probably comes from the fact that the spin-orbit coupling is not taken into account. Indeed, the spin-orbit coupling induces a decrease of the band gap value of about 1-1.3 eV. In

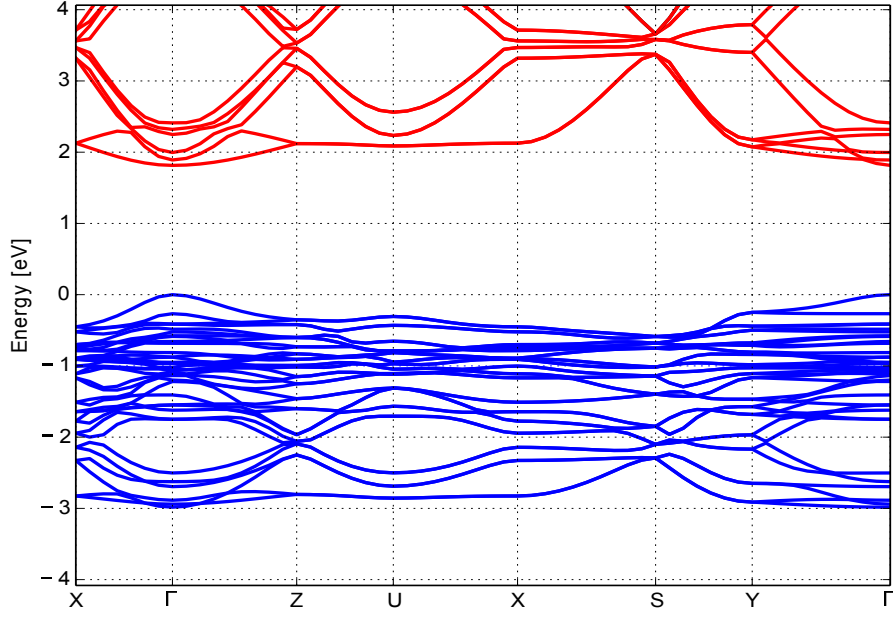


Figure 4.3: Band structure of the orthorhombic cell for specific symmetries directions in the Brillouin zone: $X - \Gamma - Z - U - X - S - Y - \Gamma$, computed with ABIPY [7]. Conduction bands are represented in red while valence bands are in blue. A band gap of 1.81 eV is found.

XCF	PBE	DFT-D3	DFT-D3(BJ)	PBE +SOC	PBE [12]
Band gap [eV]	1.815	1.738	1.667	0.58	1.61

Table 4.4: Computed band gaps for the different parameterizations: PBE, DFT-D3, DFT-D3(BJ) and PBE+SOC, compared to the experimental value reported by Baikia et al. [12].

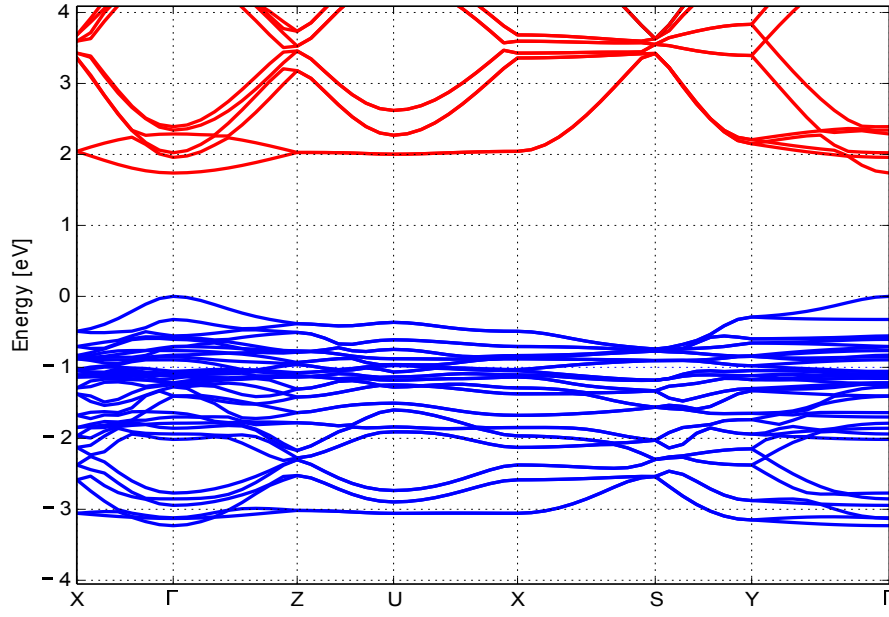
order to obtain better agreements with experiments within a fully relativistic framework, it is necessary to go beyond the Kohn-Sham Density Functional Theory by using higher order theories like GW [9].

4.2 Vibrational properties

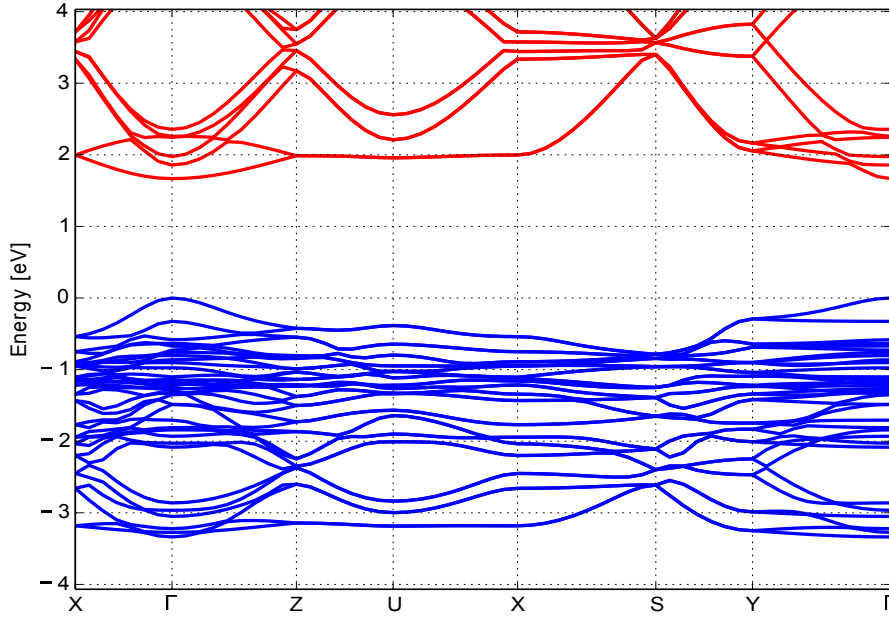
This section is devoted to the calculation and the interpretation of the normal modes of MAPbI_3 (with MA, the methylammonium cation CH_3NH_3^+) in the $Pnma$ orthorhombic structure, since in this phase the sublattice formed by the MA cations has been fully resolved via X-ray diffraction measurements [12]. The study of lattice dynamics in the two high-temperature phases, where the methylammonium cations can rotate, would require averaging over several possible orientations of the methylammonium cations, and is best addressed using molecular dynamics simulations [9].

As the spin-orbit coupling does not affect consequently the lattice parameters and the structural configuration of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ hybrid perovskite, only the sensitivity of the vibrational properties to the inclusion of van der Waals corrections is discussed.

This section is organized as follows: In section 4.2.1, the computational methods are



(a)



(b)

Figure 4.4: Band structure of the orthorhombic cell for specific symmetries directions in the Brillouin zone: $X - \Gamma - Z - U - X - S - Y - \Gamma$, computed with ABIPY [7] for (a) the DFT-D3 method and (b) the DFT-D3(BJ) method. Conduction bands are represented in red while valence bands are in blue. Band gaps of 1.74 eV and 1.67 eV are found.

introduced. In section 4.2.2, the calculated vibrational modes of $\text{CH}_3\text{NH}_3\text{PbI}_3$ are presented and each of them are decomposed into two contributions for the organic and inorganic com-

pounds, namely CH_3NH_3 , and PbI_3 respectively. Schematic representations of some characteristic modes are shown. In section 4.2.3, we proceed to a factor group analysis in order to characterize the infrared (IR) and Raman activities of each vibrational mode. Section 4.2.4 discusses the values of the Born effective charges, calculated as variations of the macroscopic electric polarization with respect to the displacement of atomic sublattices. Section 4.2.5 is devoted to the calculation of the IR absorption spectrum, based on the transverse optic (TO) modes. Finally, in sections 4.2.6 and 4.2.7, we comment on the dielectric permittivity and the LO-TO splitting. Both the dielectric permittivity and the longitudinal optic (LO) modes are closely linked to the Born effective charges, as they both depend on the mode-oscillator strength tensor defined in equation 3.104.

4.2.1 Computational parametrization

Vibrational properties are studied using density functional perturbation theory (DFPT) as implemented in ABINIT [17, 18]. The exchange and correlation energy is approximated by the PBE generalized gradient approach [66]. The core-valence interaction is described by ONCVSP-PBE norm-conserving pseudopotentials.

The convergence criteria for the lattice vibrations and dielectric properties have been set to 1% of relative difference for the Born effective charges and the dielectric tensors and 2% of relative difference with respect to asymptotic values for the phonon frequencies. The electronic wave functions have been expanded using plane waves corresponding to energies up to 50 Hartree and a 4x3x4 Monkhorst-pack grid has been chosen for sampling the Brillouin zone of the orthorhombic cell in the direct lattice, in order to get converged properties.

ABINIT gives access to various response functions that are second derivatives of the total energy with respect to different perturbations. One of these perturbations are the phonons which consist of the displacement of one atom along one of the axis of the unit cell, by a unit of length. The physical properties connected to the second derivatives of the total energy are numerous. Among them, the phonon dynamical matrix (phonon frequencies), the Born effective charges, the infrared spectrum, and the dielectric tensor are discussed.

Phonon frequencies are computed at relaxed lattice parameters. Given the relatively large unit cell, we calculate the normal vibrational modes within the harmonic approximation at the Γ point ($q = 0$). When computing the full dynamical matrix at Γ , all the atoms are displaced in all the directions. There are then $48 \cdot 3 = 144$ perturbations to be considered. Hopefully, ABINIT is able to determine which perturbations are symmetric (equivalent) to another perturbation and the Central Processing Unit (CPU) time will not be too high.

In order to get a good agreement between the calculated phonon frequencies and the experimental ones, it is needed to take the coupling between atomic displacements and an homogeneous electric field into account. The computation of responses to an electric field and to atomic displacements in a same run allows the prediction of the LO-TO splitting of the phonon frequencies. The LO-TO splitting is taken into account by evaluating the nonanalytical term of the dynamical matrix (equation 3.106).

All the calculations have been done using the ABINIT software [17, 18].

4.2.2 Phonon frequencies at the Gamma point

Atoms are bound to their equilibrium positions by the forces that hold the crystal together. When atoms are displaced from their equilibrium position, they experience a restoring force and vibrate at characteristic frequencies that are determined by the phonon modes of the crystal. The computation of these resonant frequencies is relevant for two reasons. Firstly, it

allows the computation of the frequency-dependent dielectric tensor. Secondly, as the crystal is polar, it is infrared-active and it can absorb light in the terahertz region.

Figure 4.5 shows the 144 normal vibrational modes of $\text{CH}_3\text{NH}_3\text{PbI}_3$ extending from 0 up to 3200 cm^{-1} . These 144 normal modes correspond to the number of degrees of freedom of the 4 $\text{CH}_3\text{NH}_3\text{PbI}_3$ units contained in the unit cell. Qualitatively, it is possible to distinct three energetic regions of phonons in figure 4.5: a low-frequency region from 0 to 150 cm^{-1} , (2) a mid-frequency region from 355 to 1600 cm^{-1} , and (3) a high-frequency region from 2980 to 3200 cm^{-1} . These ranges are consistent with previous computational reports [13, 50].

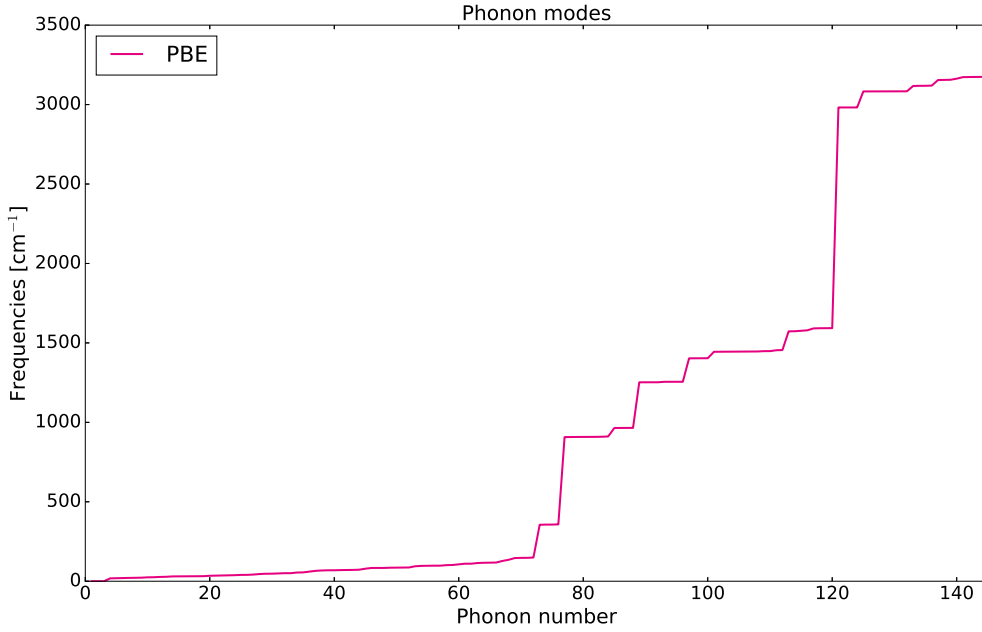
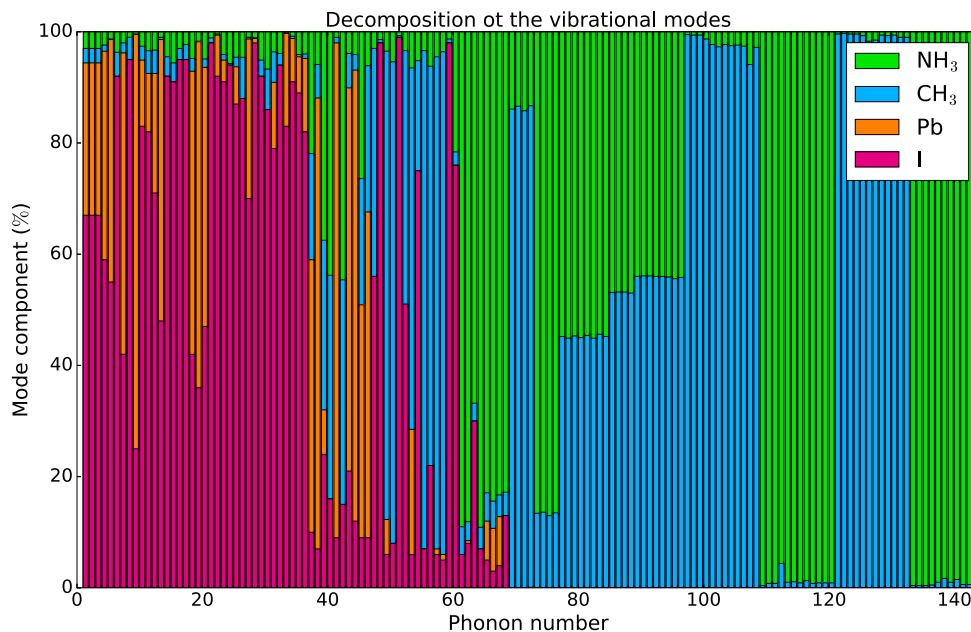


Figure 4.5: Computed vibrational frequencies of each normal mode of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in the low-temperature orthorhombic phase at the Γ point, calculated within the PBE approximation for the exchange-correlation functional.

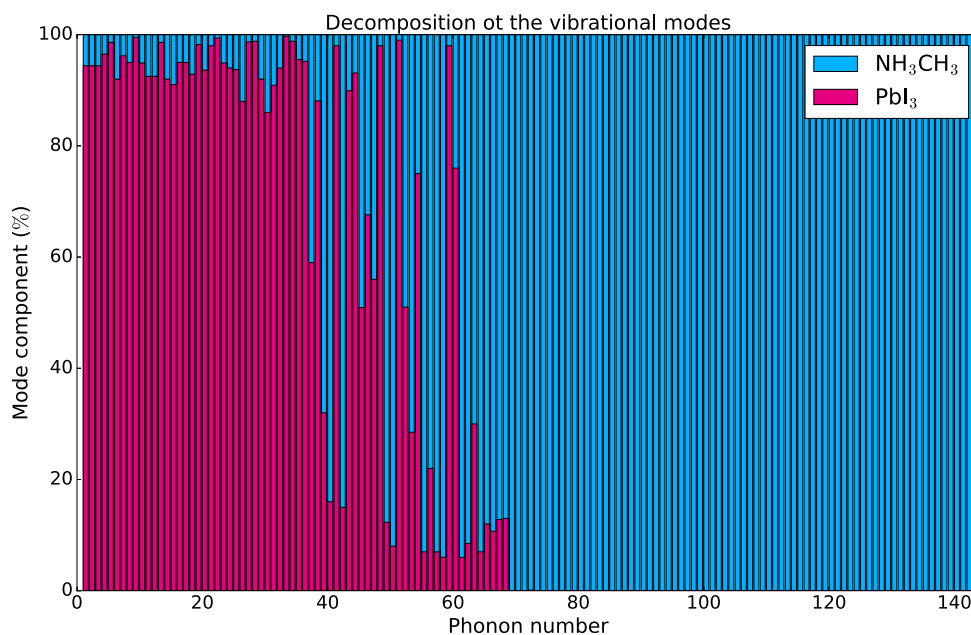
Due to the large difference in atomic mass between the organic and inorganic components, it was expected that the low frequency modes would comprise the motion of the PbI_6 octahedra, while the high frequency modes would involve the CH_3NH_3^+ cations. Thanks to a visual inspection of the atomic displacements for each mode, a decomposition of the vibrational modes of $\text{CH}_3\text{NH}_3\text{PbI}_3$ into different components corresponding to different parts of the system is performed. Figure 4.6(a) represents such decomposition into four main contributions: CH_3 , NH_3 , Pb , and I . It is possible to show (see figure 4.6(b)) that the mixing between the internal vibrational modes of the PbI_3 network and those of the MA cation is negligible [13].

The inclusion of van der Waals corrections almost keeps the shape of figure 4.5 unchanged, as represented in figure 4.7(a). The decomposition of the vibrational modes computed within the DFT-D3 (figure 4.7(b)) and DFT-D3(BJ) (figure 4.7(c)) approaches is also similar to the one performed within the PBE approximation; only some remarkable changes between 75 cm^{-1} ($\sim$ mode 40) and 360 cm^{-1} ($\sim$ mode 76) are observable, especially for DFT-D3.

The PbI_3 network admits 48 vibrational modes at Γ while MA cation admits 96 ones corresponding to the number of degrees of freedom. All the 144 normal modes are shown in table 4.5, 4.6, 4.7 for the PBE, DFT-D3, and DFT-D3(BJ) approaches, respectively.



(a)



(b)

Figure 4.6: Decomposition of the vibrational modes of the low-temperature orthorhombic phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$. The contribution to each of the vibration of (a) NH_3 , CH_3 , Pb , and I groups are represented in green, blue, orange, and pink, respectively, and of (b) CH_3NH_3 , and PbI_3 groups are represented in blue and pink, respectively.

4.2.3 Symmetry analysis and mode activity

In order to establish the symmetry of the normal modes of vibration and predict the Infrared (IR) and Raman activity, one proceeds to a group factor analysis.

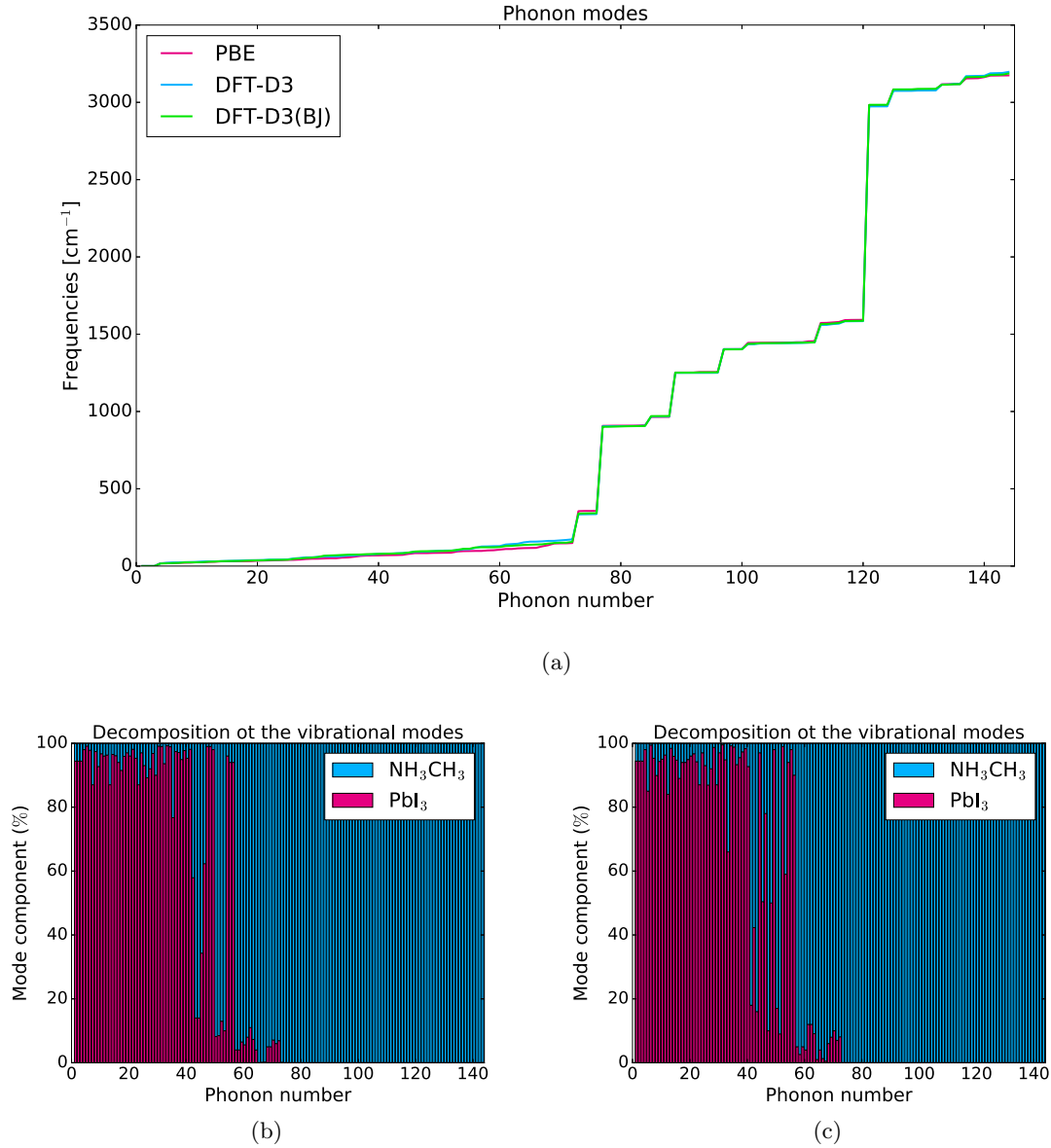


Figure 4.7: (a) Computed vibrational frequencies of each normal mode of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in the low-temperature orthorhombic phase at the Γ point, calculated within the PBE approximation (pink), the DFT-D3 method (blue), and the DFT-D3(BJ) (green). (b) and (c) Decomposition of the vibrational modes of the low-temperature orthorhombic phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$, calculated with the DFT-D3 and DFT-D3(BJ) approach, respectively.

A space group of a crystal, also called a crystallographic group, represents a description of the symmetries of the crystalline structure. In our case, the perovskite phase stable at low-temperature is the orthorhombic one. The space group (referred to as number 62) is the $Pnma$ and is bipyramidal and centrosymmetric. The Wyckoff positions of group 62 ($Pnma$) are mentioned in table 4.8.

From the reduced coordinates of each atom, it is possible to assign the different Wyckoff positions. For lead (Pb): 4a, for iodine (I): 4c and 8d, for nitrogen (N): 4c, for carbon (C): 4c, and for hydrogen (H): two times 4c and two times 8d. Therefore, we have one 4a, five 4c and three 8d. Depending on the Wyckoff positions, one can get different mechanical

mode no.	sym	active	freq [cm ⁻¹]	mode no.	sym	active	freq [cm ⁻¹]	mode no.	sym	active	freq [cm ⁻¹]
1	B_{2u}		0.0	49	B_{1u}	IR	83.7	97	A_g	Raman	1403.0
2	B_{1u}		0.0	50	B_{2g}	Raman	85.1	98	B_{3u}	IR	1403.2
3	B_{3u}		0.0	51	B_{3g}	Raman	85.6	99	B_{1u}	IR	1403.2
4	A_u	silent	18.1	52	A_g	Raman	86.4	100	B_{2g}	Raman	1403.5
5	B_{2u}	IR	18.8	53	B_{3u}	IR	86.4	101	B_{2u}	IR	1444.2
6	A_g	Raman	19.1	54	B_{1g}	Raman	94.2	102	B_{3u}	IR	1444.7
7	B_{1u}	IR	20.3	55	B_{3g}	Raman	96.6	103	B_{1g}	Raman	1444.7
8	B_{1g}	Raman	20.9	56	B_{1g}	Raman	97.3	104	B_{3g}	Raman	1444.7
9	A_u	silent	21.8	57	B_{2u}	IR	97.9	105	A_g	Raman	1444.7
10	B_{3u}	IR	22.4	58	A_u	silent	97.9	106	A_u	silent	1445.7
11	A_u	silent	25.2	59	B_{2g}	Raman	101.1	107	B_{2g}	Raman	1445.7
12	B_{1u}	IR	26.4	60	B_{3g}	Raman	102.3	108	B_{1u}	IR	1446.0
13	B_{2u}	IR	27.1	61	A_g	Raman	110.3	109	A_g	Raman	1448.2
14	B_{2g}	Raman	28.0	62	A_u	silent	110.3	110	B_{3u}	IR	1448.2
15	A_g	Raman	30.5	63	B_{3g}	Raman	114.5	111	B_{1u}	IR	1453.0
16	B_{3g}	Raman	30.5	64	B_{2g}	Raman	116.2	112	B_{2g}	Raman	1445.0
17	B_{2g}	Raman	30.8	65	B_{3u}	IR	116.6	113	B_{2u}	IR	1572.7
18	B_{3u}	IR	31.4	66	B_{2u}	IR	117.6	114	B_{1g}	Raman	1573.4
19	A_u	silent	31.7	67	B_{1u}	IR	121.4	115	B_{3g}	Raman	1576.4
20	B_{2u}	IR	31.7	68	B_{1g}	Raman	134.9	116	A_u	silent	1579.2
21	A_g	Raman	34.4	69	B_{3g}	Raman	146.0	117	B_{3u}	IR	1591.2
22	B_{3u}	IR	35.3	70	A_u	silent	147.2	118	A_g	Raman	1592.5
23	B_{1u}	IR	36.1	71	B_{1g}	Raman	147.2	119	B_{2g}	Raman	1592.5
24	B_{1g}	Raman	37.4	72	B_{2u}	IR	149.1	120	B_{1u}	IR	1592.9
25	B_{3u}	IR	39.8	73	A_u	silent	355.3	121	A_g	Raman	2981.9
26	B_{2g}	Raman	40.1	74	B_{3g}	Raman	356.5	122	B_{2g}	Raman	2981.9
27	B_{2u}	IR	42.0	75	B_{2u}	IR	356.5	123	B_{1u}	IR	2981.9
28	B_{1u}	IR	43.7	76	B_{1g}	Raman	357.9	124	B_{3u}	IR	2981.9
29	B_{3g}	Raman	45.4	77	B_{2g}	Raman	907.0	125	B_{1u}	IR	3082.9
30	A_g	Raman	47.6	78	B_{2u}	IR	908.0	126	B_{1g}	Raman	3082.9
31	B_{3u}	IR	49.0	79	B_{1u}	IR	908.0	127	A_g	Raman	3082.9
32	A_u	silent	50.6	80	A_u	silent	908.0	128	B_{2g}	Raman	3082.9
33	B_{2g}	Raman	50.6	81	A_g	Raman	908.0	129	B_{3u}	IR	3082.9
34	B_{2u}	IR	54.7	82	B_{3g}	Raman	908.6	130	B_{3g}	Raman	3082.9
35	A_u	silent	55.6	83	B_{3u}	IR	909.3	131	B_{2u}	IR	3083.4
36	B_{1u}	IR	57.3	84	B_{1g}	Raman	911.1	132	A_u	silent	3083.4
37	B_{1u}	IR	60.5	85	A_g	Raman	964.5	133	A_g	Raman	3116.9
38	B_{3u}	IR	65.4	86	B_{1u}	IR	964.9	134	B_{2g}	Raman	3118.1
39	B_{3u}	IR	67.7	87	B_{3u}	IR	964.9	135	B_{3u}	IR	3118.1
40	A_g	Raman	68.9	88	B_{2g}	Raman	964.9	136	B_{1u}	IR	3118.9
41	A_u	silent	68.9	89	A_u	silent	1252.2	137	A_u	silent	3154.5
42	B_{2g}	Raman	70.1	90	B_{2u}	IR	1252.2	138	B_{3g}	Raman	3155.2
43	B_{1u}	IR	70.6	91	B_{3g}	Raman	1252.2	139	B_{2u}	IR	3156.1
44	B_{2u}	IR	71.3	92	B_{1g}	Raman	1252.2	140	B_{1g}	Raman	3163.1
45	B_{1u}	IR	75.7	93	A_g	Raman	1255.2	141	A_g	Raman	3172.7
46	B_{3u}	IR	79.0	94	B_{1u}	IR	1255.2	142	B_{3u}	IR	3173.5
47	A_g	Raman	83.7	95	B_{3u}	IR	1255.2	143	B_{1u}	IR	3173.5
48	B_{1g}	Raman	83.7	96	B_{2g}	Raman	1255.2	144	B_{2g}	Raman	3174.1

Table 4.5: Frequency, symmetry and activity of the normal vibration modes of MAPbI₃ in the low-temperature orthorhombic phase at the Γ point.

representations defining the type of modes. The mechanical representation is defined as the direct product of the permutational representation with the vectorial representation. Such representation is given in table 4.9 for the $Pnma$ structure of CH₃NH₃PbI₃.

In summary, the perovskite CH₃NH₃PbI₃ admits 144 vibrational modes at Γ corresponding to the displacements along the three directions for each of the 48 atoms included in the unit cell. These 144 normal modes include 3 pure translation modes called the acoustic modes, and 141 optical modes. The irreducible representation of normal modes is given by

mode no.	sym	active	freq [cm ⁻¹]	mode no.	sym	active	freq [cm ⁻¹]	mode no.	sym	active	freq [cm ⁻¹]
1	B_{2u}		0.0	49	A_g	Raman	93.2	97	B_{1u}	IR	1403.7
2	B_{1u}		0.0	50	B_{1u}	IR	98.1	98	B_{2g}	Raman	1403.7
3	B_{3u}		0.0	51	B_{3u}	IR	98.9	99	A_g	Raman	1403.7
4	A_u	silent	16.8	52	B_{2g}	Raman	100.2	100	B_{3u}	IR	1403.7
5	B_{2u}	IR	21.0	53	A_g	Raman	100.5	101	A_g	Raman	1435.2
6	B_{3u}	IR	22.8	54	B_{1g}	Raman	101.7	102	B_{3u}	IR	1435.7
7	A_g	Raman	23.1	55	B_{2g}	Raman	108.6	103	B_{1u}	IR	1439.6
8	A_u	silent	25.2	56	B_{3g}	Raman	109.3	104	B_{2g}	Raman	1440.3
9	B_{1u}	IR	25.2	57	B_{3g}	Raman	126.6	105	B_{3u}	IR	1440.6
10	B_{2u}	IR	26.9	58	B_{1g}	Raman	127.2	106	A_g	Raman	1440.9
11	B_{1g}	Raman	29.1	59	B_{2u}	IR	128.7	107	B_{2u}	IR	1442.5
12	B_{1u}	IR	30.4	60	A_u	silent	129.1	108	B_{3g}	Raman	1442.9
13	B_{2g}	Raman	30.4	61	A_u	silent	139.4	109	B_{1g}	Raman	1443.3
14	A_u	silent	30.4	62	B_{3g}	Raman	142.0	110	A_u	silent	1444.0
15	B_{2u}	IR	31.6	63	B_{2u}	IR	144.8	111	B_{1u}	IR	1444.7
16	A_g	Raman	32.8	64	B_{1g}	Raman	153.5	112	B_{2g}	Raman	1446.8
17	B_{3u}	IR	33.5	65	B_{3g}	Raman	157.9	113	B_{2u}	IR	1559.9
18	A_u	silent	35.0	66	A_u	silent	158.2	114	B_{1g}	Raman	1560.4
19	B_{2g}	Raman	37.4	67	B_{2u}	IR	159.9	115	B_{3g}	Raman	1565.5
20	B_{3g}	Raman	37.7	68	B_{1g}	Raman	162.9	116	A_u	silent	1568.3
21	B_{3u}	IR	37.7	69	A_g	Raman	163.3	117	B_{3u}	IR	1583.4
22	B_{1u}	IR	40.2	70	B_{3u}	IR	165.8	118	B_{2g}	Raman	1583.7
23	B_{2g}	Raman	41.4	71	B_{2g}	Raman	169.1	119	B_{1u}	IR	1584.5
24	A_g	Raman	41.8	72	B_{1u}	IR	171.0	120	A_g	Raman	1584.5
25	B_{1g}	Raman	43.2	73	A_u	silent	334.3	121	A_g	Raman	2974.0
26	B_{3u}	IR	49.2	74	B_{2u}	IR	334.8	122	B_{2g}	Raman	2974.0
27	B_{3g}	Raman	52.2	75	B_{3g}	Raman	335.1	123	B_{3u}	IR	2974.0
28	B_{1u}	IR	53.2	76	B_{1g}	Raman	336.3	124	B_{1u}	IR	2974.0
29	A_g	Raman	56.5	77	B_{2g}	Raman	904.1	125	B_{1u}	IR	3074.4
30	B_{2u}	IR	59.4	78	B_{2u}	IR	904.4	126	B_{2g}	Raman	3074.4
31	B_{2g}	Raman	61.7	79	A_g	Raman	904.7	127	B_{3u}	IR	3074.4
32	B_{3u}	IR	62.2	80	A_u	silent	904.7	128	A_g	Raman	3074.4
33	A_u	silent	62.6	81	B_{1u}	IR	905.2	129	B_{1g}	Raman	3076.3
34	B_{2u}	IR	64.4	82	B_{3g}	Raman	905.9	130	B_{3g}	Raman	3076.3
35	B_{1u}	IR	68.3	83	B_{3u}	IR	906.4	131	B_{2u}	IR	3076.9
36	A_u	silent	69.3	84	B_{1g}	Raman	908.1	132	A_u	silent	3076.9
37	B_{1u}	IR	70.3	85	A_g	Raman	967.1	133	B_{3u}	IR	3115.1
38	B_{3u}	IR	71.9	86	B_{3u}	IR	967.6	134	A_g	Raman	3115.7
39	A_u	silent	73.3	87	B_{1u}	IR	967.6	135	B_{1u}	IR	3118.8
40	B_{1u}	IR	76.6	88	B_{2g}	Raman	967.6	136	B_{2g}	Raman	3119.1
41	B_{2u}	IR	78.8	89	B_{2g}	Raman	1249.7	137	B_{2g}	Raman	3169.6
42	B_{3u}	IR	79.7	90	B_{3u}	IR	1249.7	138	B_{1u}	IR	3169.6
43	A_g	Raman	81.1	91	B_{1g}	Raman	1250.1	139	A_g	Raman	3170.5
44	B_{2g}	Raman	82.8	92	A_g	Raman	1250.1	140	B_{3u}	IR	3171.9
45	B_{1u}	IR	85.6	93	B_{2u}	IR	1250.1	141	A_u	silent	3187.9
46	B_{3u}	IR	87.0	94	B_{1u}	IR	1250.1	142	B_{3g}	Raman	3188.7
47	B_{1g}	Raman	91.6	95	A_u	silent	1250.1	143	B_{2u}	IR	3190.0
48	B_{3g}	Raman	92.7	96	B_{3g}	Raman	1250.5	144	B_{1g}	Raman	3196.8

Table 4.6: Frequency, symmetry and activity of the normal vibration modes of MAPbI₃ in the low-temperature orthorhombic phase at the Γ point, calculated with DFT-D3.

the theoretical group analysis:

$$\Gamma = 17A_u + 22B_{1u} + 17B_{2u} + 22B_{3u} + 19A_g + 14B_{1g} + 19B_{2g} + 14B_{3g} \quad (4.2)$$

These different modes have been identified thanks to the associated character table by directly applying the appropriate symmetry operations. We have 8 symmetry operations including the identity (1), the inversion ($\bar{1}$), three second order rotations ($2_x, 2_y, 2_z$), and three mirror planes (m_x, m_y, m_z). The character table allowing to link these operations to the

mode no.	sym	active	freq [cm ⁻¹]	mode no.	sym	active	freq [cm ⁻¹]	mode no.	sym	active	freq [cm ⁻¹]
1	<i>B</i> _{2u}		0.0	49	<i>B</i> _{1g}	Raman	96.3	97	<i>A</i> _g	Raman	1401.7
2	<i>B</i> _{1u}		0.0	50	<i>B</i> _{2g}	Raman	97.1	98	<i>B</i> _{1u}	IR	1401.7
3	<i>B</i> _{3u}		0.0	51	<i>B</i> _{3u}	IR	97.1	99	<i>B</i> _{2g}	Raman	1402.1
4	<i>A</i> _u	silent	16.5	52	<i>B</i> _{3g}	Raman	97.6	100	<i>B</i> _{3u}	IR	1402.1
5	<i>A</i> _g	Raman	17.5	53	<i>A</i> _g	Raman	99.1	101	<i>A</i> _g	Raman	1437.7
6	<i>B</i> _{2u}	IR	19.4	54	<i>B</i> _{1g}	Raman	105.4	102	<i>B</i> _{3u}	IR	1438.0
7	<i>B</i> _{3u}	IR	20.3	55	<i>B</i> _{2g}	Raman	111.3	103	<i>B</i> _{2g}	Raman	1442.2
8	<i>B</i> _{1u}	IR	22.9	56	<i>B</i> _{3g}	Raman	112.0	104	<i>B</i> _{1u}	IR	1442.2
9	<i>A</i> _u	silent	23.8	57	<i>B</i> _{1g}	Raman	121.6	105	<i>A</i> _g	Raman	1442.6
10	<i>B</i> _{1g}	Raman	24.7	58	<i>B</i> _{3g}	Raman	121.6	106	<i>B</i> _{3u}	IR	1442.6
11	<i>B</i> _{2u}	IR	25.2	59	<i>A</i> _u	silent	121.6	107	<i>B</i> _{2u}	IR	1443.6
12	<i>B</i> _{2g}	Raman	28.0	60	<i>B</i> _{2u}	IR	123.2	108	<i>B</i> _{3g}	Raman	1444.0
13	<i>A</i> _u	silent	28.9	61	<i>A</i> _u	silent	129.7	109	<i>B</i> _{1g}	Raman	1444.3
14	<i>B</i> _{2u}	IR	31.6	62	<i>B</i> _{3g}	Raman	131.0	110	<i>A</i> _u	silent	1445.3
15	<i>B</i> _{1u}	IR	31.6	63	<i>B</i> _{2u}	IR	133.7	111	<i>B</i> _{1u}	IR	1445.3
16	<i>A</i> _g	Raman	32.6	64	<i>B</i> _{1g}	Raman	136.9	112	<i>B</i> _{2g}	Raman	1447.4
17	<i>B</i> _{3u}	IR	32.6	65	<i>B</i> _{3g}	Raman	138.4	113	<i>B</i> _{2u}	IR	1565.2
18	<i>B</i> _{3g}	Raman	33.1	66	<i>A</i> _u	silent	139.2	114	<i>B</i> _{1g}	Raman	1565.7
19	<i>A</i> _u	silent	34.5	67	<i>B</i> _{2u}	IR	140.7	115	<i>B</i> _{3g}	Raman	1569.5
20	<i>B</i> _{2g}	Raman	35.5	68	<i>A</i> _g	Raman	145.6	116	<i>A</i> _u	silent	1572.8
21	<i>B</i> _{3u}	IR	37.6	69	<i>B</i> _{3u}	IR	149.1	117	<i>B</i> _{3u}	IR	1585.0
22	<i>B</i> _{1u}	IR	38.8	70	<i>B</i> _{2g}	Raman	151.1	118	<i>B</i> _{2g}	Raman	1585.9
23	<i>A</i> _g	Raman	39.7	71	<i>B</i> _{1g}	Raman	151.1	119	<i>A</i> _g	Raman	1586.2
24	<i>B</i> _{2g}	Raman	39.7	72	<i>B</i> _{1u}	IR	154.0	120	<i>B</i> _{1u}	IR	1596.5
25	<i>B</i> _{1g}	Raman	40.9	73	<i>A</i> _u	silent	339.9	121	<i>B</i> _{1u}	IR	2984.2
26	<i>B</i> _{3u}	IR	46.5	74	<i>B</i> _{2u}	IR	340.7	122	<i>B</i> _{3u}	IR	2984.2
27	<i>B</i> _{3g}	Raman	50.0	75	<i>B</i> _{3g}	Raman	341.1	123	<i>A</i> _g	Raman	2984.2
28	<i>B</i> _{1u}	IR	52.3	76	<i>B</i> _{1g}	Raman	342.2	124	<i>B</i> _{2g}	Raman	2984.2
29	<i>A</i> _g	Raman	52.7	77	<i>B</i> _{2u}	IR	901.0	125	<i>A</i> _g	Raman	3083.8
30	<i>B</i> _{2g}	Raman	58.5	78	<i>A</i> _u	silent	901.3	126	<i>B</i> _{2g}	Raman	3083.8
31	<i>B</i> _{2u}	IR	66.9	79	<i>B</i> _{3g}	Raman	902.5	127	<i>B</i> _{3u}	IR	3083.8
32	<i>B</i> _{3u}	IR	68.0	80	<i>B</i> _{2g}	Raman	903.7	128	<i>B</i> _{1u}	IR	3083.8
33	<i>B</i> _{1u}	IR	69.6	81	<i>A</i> _g	Raman	904.5	129	<i>B</i> _{1g}	Raman	3087.0
34	<i>A</i> _u	silent	71.9	82	<i>B</i> _{1g}	Raman	904.9	130	<i>B</i> _{3g}	Raman	3087.0
35	<i>B</i> _{2u}	IR	73.8	83	<i>B</i> _{1u}	IR	905.2	131	<i>A</i> _u	silent	3087.6
36	<i>B</i> _{1u}	IR	74.2	84	<i>B</i> _{3u}	IR	906.2	132	<i>B</i> _{2u}	IR	3087.6
37	<i>B</i> _{3u}	IR	74.2	85	<i>A</i> _g	Raman	970.2	133	<i>B</i> _{3u}	IR	3113.6
38	<i>A</i> _u	silent	74.8	86	<i>B</i> _{2g}	Raman	970.6	134	<i>A</i> _g	Raman	3114.1
39	<i>A</i> _u	silent	77.0	87	<i>B</i> _{1u}	IR	970.6	135	<i>B</i> _{2g}	Raman	3117.2
40	<i>B</i> _{1u}	IR	79.3	88	<i>B</i> _{3u}	IR	970.6	136	<i>B</i> _{1u}	IR	3117.2
41	<i>A</i> _g	Raman	79.6	89	<i>B</i> _{1g}	Raman	1251.2	137	<i>B</i> _{2g}	Raman	3162.9
42	<i>B</i> _{2g}	Raman	79.9	90	<i>B</i> _{2u}	IR	1251.2	138	<i>A</i> _g	Raman	3163.2
43	<i>B</i> _{3u}	IR	79.9	91	<i>A</i> _u	silent	1251.2	139	<i>B</i> _{1u}	IR	3163.2
44	<i>B</i> _{2u}	IR	82.0	92	<i>B</i> _{3g}	Raman	1251.6	140	<i>B</i> _{3u}	IR	3165.3
45	<i>B</i> _{1u}	IR	84.3	93	<i>B</i> _{2g}	Raman	1253.3	141	<i>A</i> _u	silent	3177.6
46	<i>B</i> _{3u}	IR	87.6	94	<i>B</i> _{3u}	IR	1253.3	142	<i>B</i> _{3g}	Raman	3178.4
47	<i>B</i> _{1u}	IR	94.9	95	<i>A</i> _g	Raman	1253.5	143	<i>B</i> _{2u}	IR	3179.3
48	<i>A</i> _g	Raman	95.9	96	<i>B</i> _{1u}	IR	1253.5	144	<i>B</i> _{1g}	Raman	3186.5

Table 4.7: Frequency, symmetry and activity of the normal vibration modes of MAPbI₃ in the low-temperature orthorhombic phase at the Γ point, calculated with DFT-D3(BJ).

vibrational modes is shown in table 4.10.

In order to predict which vibrational modes will be IR active, Raman active or inactive, the symmetry properties of these modes will be needed. A mode is IR active when a dipole moment is induced due to the change in atomic positions while it is Raman active when a dipole moment is induced due to the deformation of the electron shell. The infrared

Multiplicity	Wyckoff letter	Site symmetry	Coordinates
8	d	1	$(x, y, z), (-x + 1/2, -y, z + 1/2), (-x, y + 1/2, -z),$ $(x + 1/2, -y + 1/2, -z + 1/2), (-x, -y, -z),$ $(x + 1/2, y, -z + 1/2), (x, -y + 1/2, z),$ $(-x + 1/2, y + 1/2, z + 1/2)$
4	c	m	$(x, 1/4, z), (-x + 1/2, 3/4, z + 1/2), (-x, 3/4, -z),$ $(x + 1/2, 1/4, -z + 1/2)$
4	b	-1	$(0, 0, 1/2), (1/2, 0, 0), (0, 1/2, 1/2), (1/2, 1/2, 0)$
4	a	-1	$(0, 0, 0), (1/2, 0, 1/2), (0, 1/2, 0), (1/2, 1/2, 1/2)$

 Table 4.8: Wyckoff positions of group 62 (*Pnma*) [6].

WP	A _g	A _u	B _{1g}	B _{1u}	B _{2g}	B _{2u}	B _{3g}	B _{3u}
4a	0	3	0	3	0	3	0	3
4c	2	1	1	2	2	1	1	2
8d	3	3	3	3	3	3	3	3

 Table 4.9: Mechanical representation of the space group *Pnma* (62) [6].

	1	2 _z	2 _y	2 _x	$\bar{1}$	m _z	m _y	m _x	functions
A _g	1	1	1	1	1	1	1	1	x ² , y ² , z ²
B _{1g}	1	1	-1	-1	1	1	-1	-1	xy, J _z
B _{2g}	1	-1	1	-1	1	-1	1	-1	xz, J _y
B _{3g}	1	-1	-1	1	1	-1	-1	1	yz, J _x
A _u	1	1	1	1	-1	-1	-1	-1	
B _{1u}	1	1	-1	-1	-1	-1	1	1	z
B _{2u}	1	-1	1	-1	-1	1	-1	1	y
B _{3u}	1	-1	-1	1	-1	1	1	-1	x

 Table 4.10: Character table of the space group *Pnma* (62) [6]. The first column corresponds to the irreducible representations, the eight next columns correspond to the symmetry operations and the last column contains the selection rules.

intensities are proportional to the change in the electric dipole μ :

$$I_{\text{IR}} \propto \left| \left(\frac{\partial \mu}{\partial Q_k} \right)_0 \right|^2$$

The Raman intensities are proportional to the change in polarization P (dipole moment per unit cell) with $P = \alpha \cdot E$ where E is the electric field and α is the polarizability tensor:

$$I_{\text{Raman}} \propto \left| e_s \left(\frac{\partial \alpha}{\partial Q_k} \right)_0 e_i \right|^2$$

In our case, the IR dipole moments and Raman tensors of each irreducible representation are given in table 4.11.

According to table 4.11 and using the matrix element theorem, one can say that a mode will be IR active if its eigenmode belongs to one of the irreducible representations of the electric dipole operator, which means that, in the case of orthorhombic MAPbI₃, only the B_{1u} , B_{2u} , and B_{3u} modes will be IR active as the representation of the dipole is

$$B_{1u} \oplus B_{2u} \oplus B_{3u}$$

Irreducible representations	Electric dipole operator μ (IR)	Polarizability tensor α (Raman)
A_g	$\mu = (0, 0, 0)$	$\alpha = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}$
B_{1g}	$\mu = (0, 0, 0)$	$\alpha = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$
B_{2g}	$\mu = (0, 0, 0)$	$\alpha = \begin{pmatrix} 0 & 0 & e \\ 0 & 0 & 0 \\ e & 0 & 0 \end{pmatrix}$
B_{3g}	$\mu = (0, 0, 0)$	$\alpha = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & f \\ 0 & f & 0 \end{pmatrix}$
A_u	$\mu = (0, 0, 0)$	$\alpha = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$
B_{1u}	$\mu = (0, 0, \mu_z)$	$\alpha = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$
B_{2u}	$\mu = (0, \mu_y, 0)$	$\alpha = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$
B_{3u}	$\mu = (\mu_x, 0, 0)$	$\alpha = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$

 Table 4.11: IR dipole moments μ and Raman tensors α of each irreducible representation.

In the same way, a mode will be Raman active if its displacement pattern belongs to one of the irreducible representations of the polarizability tensor, which means that, in the case of orthorhombic MAPbI₃, only the B_{1g} , B_{2g} , B_{3g} , and A_g modes will be Raman active as the representation of the polarizability is

$$B_{1g} \oplus B_{2g} \oplus B_{3g} \oplus A_g$$

Equation 4.2 can therefore be rewritten as:

$$\Gamma_{\text{acoustic}} = B_{1u} + B_{2u} + B_{3u} \quad (4.3)$$

$$\Gamma_{\text{optic}} = 17A_u + \underbrace{21B_{1u} + 16B_{2u} + 21B_{3u}}_{\text{IR active}} + \underbrace{19A_g + 14B_{1g} + 19B_{2g} + 14B_{3g}}_{\text{Raman active}} \quad (4.4)$$

The remaining A_u normal modes are expected to be silent as their irreducible representation is not contained neither in the representation of the electric dipole operator nor in the representation of the polarizability tensor [13].

Tables 4.5, 4.6, and 4.7 reported all the calculated vibrational TO frequencies of each mode, their IR or Raman activity, and their symmetry group for the PBE, DFT-D3, and DFT-D3(BJ) parametrization, respectively. A visual inspection allows to characterize the different vibrational modes. The first 48 normal modes correspond mostly to internal vibrations of the PbI₃ network. Normal modes related to the CH₃NH₃ cations correspond either to rigid-body motions (frequencies between 55 and 150 cm⁻¹) or are exclusively internal vibrations (frequencies higher than 355 cm⁻¹). Schematic representations of characteristic vibrational modes are provided in figure 4.8.

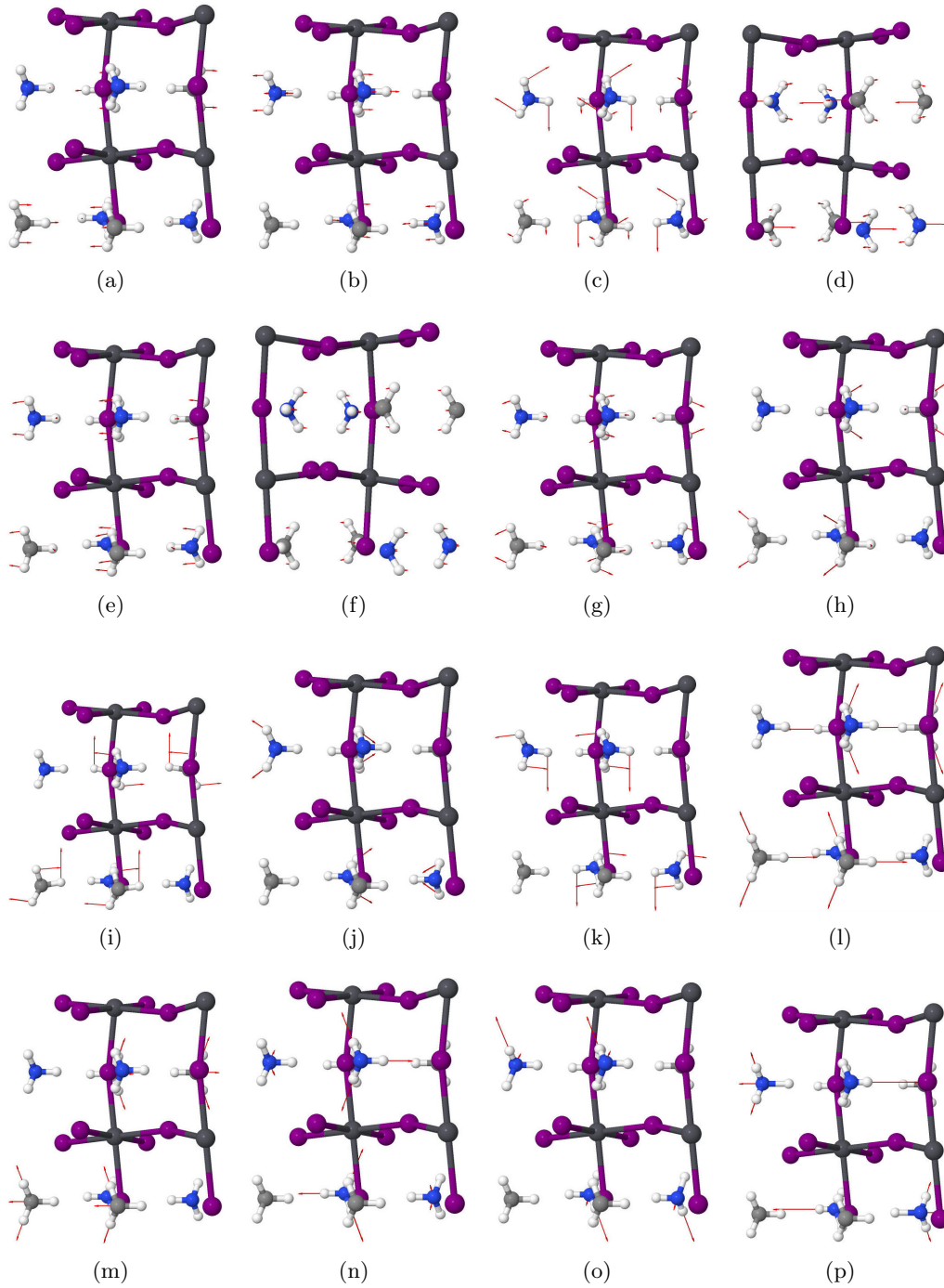


Figure 4.8: Schematic representation of some characteristic vibrational modes of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in the low-temperature orthorhombic phase. The Pb atoms are in grey and the I atoms are in purple, while the N, C and H atoms are in blue, light grey, and white, respectively. The vibrational modes (numbers are indicated) represented correspond to: (a) 49 = Translation, (b) 67 = Translation, (c) 73-76 = Torsion, (d) 77-80 = CH_3NH_3 rocking, (e) 81-84 = CH_3NH_3 rocking, (f) 85-88 = C-N stretching, (g) 89-96 = CH_3NH_3 rocking, (h) 97-100 = Symmetric CH_3 bending, (i) 101-108 = Asymmetric CH_3 bending, (j) 109-112 Symmetric NH_3 bending, (k) 113-120 Asymmetric NH_3 bending, (l) 121-124 = Symmetric C-H stretching, (m) 125-132 = Asymmetric C-H stretching, (n) 133-136 = Symmetric N-H stretching, (o) 137-140 = Asymmetric N-H stretching, (p) 141-144 = Asymmetric N-H stretching.

4.2.4 Born-effective charges

The Born effective charge tensors are calculated as variations of the macroscopic electric polarization with respect to the displacement of atomic sublattices, using the modern theory of polarization:

$$Z_{\kappa,\alpha\beta}^* = \frac{\Omega}{e} \frac{\partial P_\alpha}{\partial u_{\kappa\beta}}$$

where κ labels the atoms in the unit cell, α and β indicate cartesian directions, Ω is the unit cell volume, and e is the electron charge. P is the macroscopic polarization (dipole per unit cell) and u_κ an atomic displacement from equilibrium. We note that $Z_{\kappa,\alpha\beta}^*$ is by definition dimensionless.

The calculated Born effective tensors of the Pb atoms are found to be almost diagonal and isotropic. The isotropic average is $\frac{1}{3} \sum_\alpha Z_{\alpha\alpha}^* = +4.42$, the largest deviation from this value along the diagonal is 0.29, and the largest off-diagonal element is 0.726. The Born charge of Pb is significantly larger than the nominal ionic charge +2, which indicates that perovskites have a mixed covalent-ionic bonding character [13].

The calculated effective charge tensors of the I atoms are highly anisotropic with diagonal elements of -3.93, -0.85, -0.65, and the largest off-diagonal component equal to 0.15. The largest component is along the direction of the Pb-I bond, as expected [13]. The isotropic average of the Born effective charges of the I atoms is found to be -1.89. This value is considerably larger than the nominal charge of -1, which confirms the mixed character of the Pb-I bonding.

For the MA cations, only the isotropic averages of the Born charge tensors are discussed. We respectively find $\frac{1}{3} \sum_\alpha Z_{\alpha\alpha,C}^* = +0.17$ and $\frac{1}{3} \sum_\alpha Z_{\alpha\alpha,N}^* = -0.75$, for the carbon and nitrogen atoms. The Born effective charges associated to hydrogen atoms depend on the bonding. The hydrogen atoms associated with C atoms carry effective charges of +0.1, while those associated with N atoms carry effective charges of +0.5.

If we take the sum of the isotropic components of the Born charges for -CH₃ and for -NH₃ separately, we find +0.47 and +0.75 respectively. Therefore, the MA cations carry a Born effective charge $Z_{\text{CH}_3\text{NH}_3}^* = 0.47 + 0.75 = +1.22$. We also note that the total isotropic Born charge of the PbI₃ network is -1.24, and this is compensated by the total charge of each cation +1.22. The fact that these values are close to the nominal charges indicates that the covalent interaction between these two components is essentially negligible [13].

The total Born effective charge tensor of the unit cell is almost equal to zero and its absolute value decreases when including the van der Waals interactions, which means that the DFT-D3 and DFT-D3(BJ) approaches lead to more realistic descriptions of the perovskite structure. The calculated Born effective charges are summarized in Table 4.12.

4.2.5 Calculated infrared absorption spectrum

The IR spectrum of CH₃NH₃PbI₃ is simulated with the analytic formula of Gianozzi and Baroni (using the Born effective charge tensor) [116]. The IR intensity is given by:

$$I_{\text{IR}} = \omega \cdot \text{Im}\epsilon(\omega) = \frac{4\pi}{3\Omega} \sum_m \frac{S_{m,\alpha\alpha'}}{\omega - \omega_m} \quad (4.5)$$

with $S_{m,\alpha\alpha'}$ defined in equation 3.104, m the sum over all the modes, and α and α' referring to the cartesian directions. Based on the IR intensities, the graph for the absorbance has been plot using a Gaussian broadening:

$$\text{Abs} = \frac{4\pi}{3\Omega} \sum_m \frac{S_{m,\alpha\alpha'}}{\omega - \omega_m} \exp\left(-\frac{(\omega - \omega_m)^2}{2\sigma^2}\right) \quad (4.6)$$

XCF	PBE	DFT-D3	DFT-D3(BJ)	LDA [13]
$\overline{Z}_{\text{Pb}}^*$	+4.420	+4.232	+4.390	+4.42
$\overline{Z}_{\text{I}}^*$	-1.887	-1.796	-1.817	-1.88
$\overline{Z}_{\text{N}}^*$	-0.752	-0.827	-0.825	-0.95
$\overline{Z}_{\text{C}}^*$	+0.173	+0.120	+0.127	+0.03
$\overline{Z}_{\text{HN}}^*$	+0.499	+0.511	+0.511	+0.55
$\overline{Z}_{\text{HC}}^*$	+0.100	+0.105	+0.103	+0.13
$\overline{Z}_{\text{PbI}_3}^*$	-1.241	-1.157	-1.161	-1.22
$\overline{Z}_{\text{CH}_3\text{NH}_3}^*$	+1.218	+1.141	+1.144	+1.12
$\overline{Z}_{\text{Tot}}^*$	-0.023	-0.016	-0.017	-0.10

Table 4.12: Calculated Born effective charges of the low-temperature orthorhombic MAPbI₃ and its constituents. $\overline{Z}^* = \frac{1}{3} \sum_{\alpha} Z_{\alpha\alpha}^*$ is the isotropic average of the Born charges tensors. A comparison with values calculated with LDA is also provided [13].

where σ is the broadening and is fixed to 5. The IR spectrum is based on the TO normal modes presented in table 4.5 and is shown in figure 4.9 for the PBE approximation to the exchange-correlation functional.

The contributions from the 3 directions are also represented in dotted lines. The analysis of the IR spectrum of CH₃NH₃PbI₃ indicates three well-distinct regions. In the high-frequency range (between 3000 and 3250 cm⁻¹) and the mid-frequency range (between 800 and 1700 cm⁻¹), the infrared activity is due to the internal vibrations of the MA cations: C-H, N-H, N-C stretching modes, NH₃ and CH₃ bending modes, and CH₃NH₃ rocking modes. When analyzing the infrared activity in the low-frequency range, two distinct origins are highlighted: the rigid-body motions of the MA cations between 100 and 200 cm⁻¹, and the vibrations of the PbI₃ network for frequencies lower than 100 cm⁻¹. As already mentioned, all the peaks in the IR spectrum correspond to B_{1u}, B_{2u}, or B_{3u} symmetry.

The inclusion of van der Waals interactions modify the computed phonon frequencies in the following way: low frequencies are shifted to the right by at most 25 cm⁻¹ when coupling the PBE approximation with the DFT-D3 and DFT-D3(BJ) methods. The mid-frequency range is not consequently modified as the frequencies do not vary by more than 8 cm⁻¹. Finally, at high frequencies, both the DFT-D3 and DFT-D3(BJ) corrections give rise to a shift to the right of 20 cm⁻¹. These observations are based on the computed phonon frequencies summarized in tables 4.5, 4.6, and 4.7. Besides, it is also possible to observe these effects in the infrared spectra shown in figure 4.10 or even better in figure 4.11.

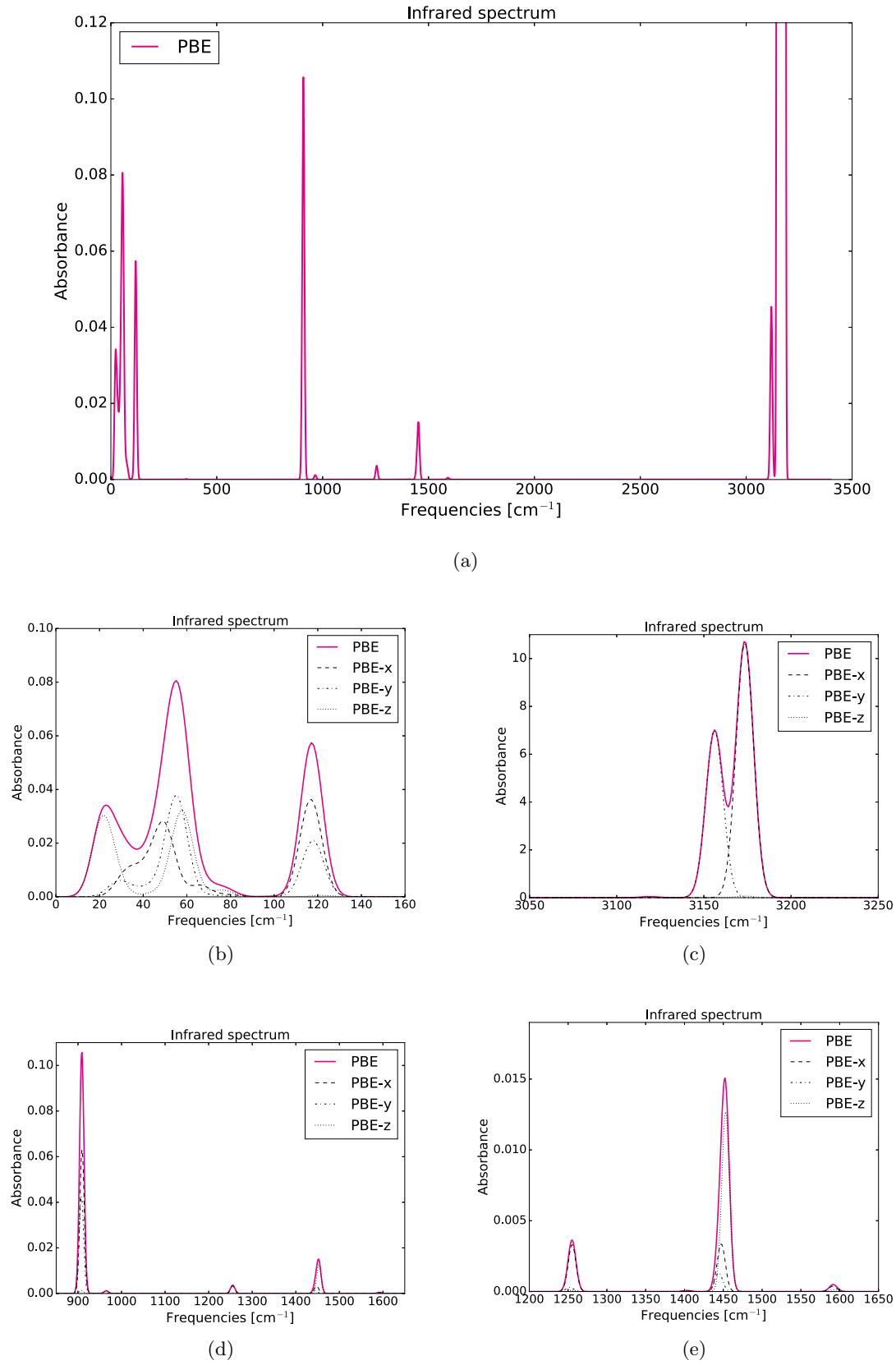


Figure 4.9: Computed infrared spectrum calculated for the low-temperature orthorhombic phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$. Based on the IR intensities, the graph has been broadened using a Gaussian function. (a) Total IR spectrum, (b), (c), and (d) correspond to the low-frequency, high-frequency, mid-frequency range and (e) is a zoom of the mid-frequency range.

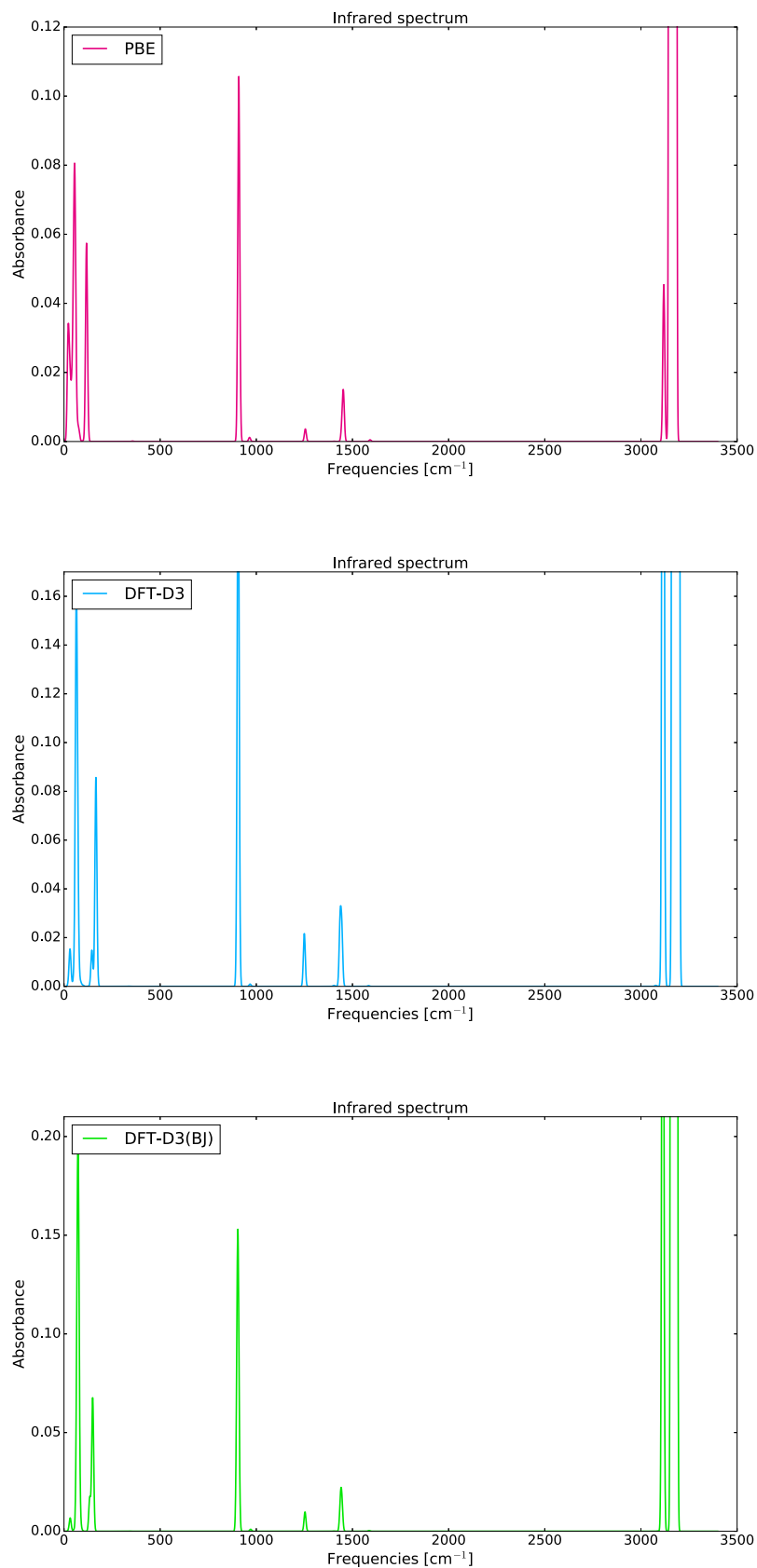


Figure 4.10: Computed infrared spectra calculated for the low-temperature orthorhombic phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$, respectively with the PBE parametrization, the DFT-D3 method, and the DFT-D3(BJ) method. Based on the IR intensities, the graph has been broadened using a Gaussian function.

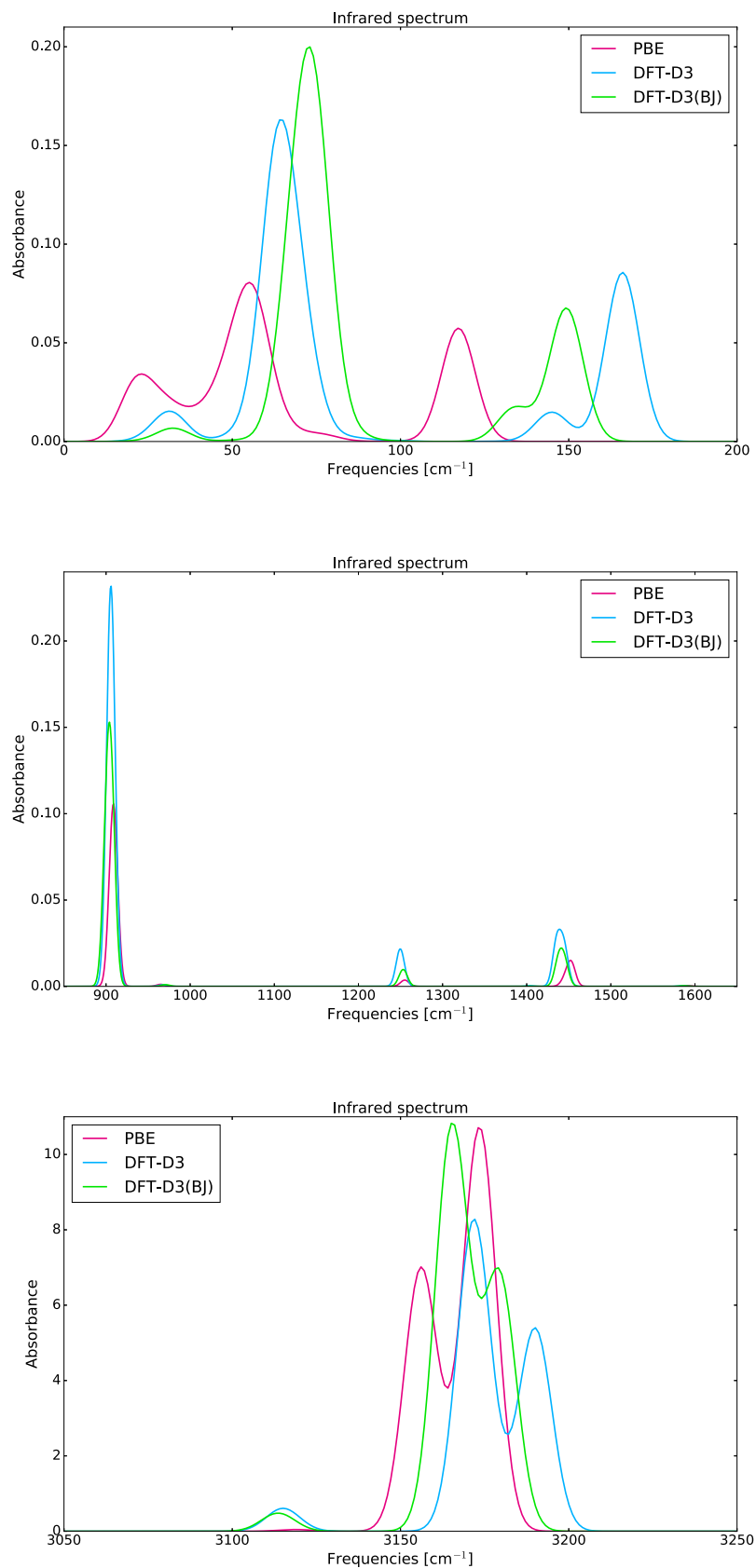


Figure 4.11: Comparison between the computed infrared spectra calculated with PBE (pink), DFT-D3 (blue), and DFT-D3(BJ) (green) for the low-temperature orthorhombic phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$, showing the low-frequency, mid-frequency, and high-frequency ranges, respectively.

4.2.6 Dielectric permittivities

The IR absorption spectrum is closely linked to the Born effective charges, and hence, to the frequency-dependent dielectric permittivity. The dielectric permittivities are computed for the low-temperature orthorhombic phase of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite.

Orthorhombic materials are not isotropic and their dielectric tensor takes the form of a diagonal matrix with three different terms in its diagonal:

$$\epsilon(\omega) = \begin{pmatrix} \epsilon_a(\omega) & 0 & 0 \\ 0 & \epsilon_b(\omega) & 0 \\ 0 & 0 & \epsilon_c(\omega) \end{pmatrix}$$

where ϵ_a , ϵ_b , and ϵ_c are components parallel and perpendicular to the a axis, respectively.

Our calculations yield a high-frequency dielectric tensor:

$$\epsilon(\infty) = \begin{pmatrix} 5.14 & 0 & 0 \\ 0 & 4.58 & 0 \\ 0 & 0 & 5.22 \end{pmatrix}$$

In order to compare our results with experimental data, we average the values parallel and perpendicular to the a axis:

$$\overline{\epsilon^\infty} = \frac{\epsilon_x^\infty + \epsilon_y^\infty + \epsilon_z^\infty}{3}$$

This average does not really have any physical meaning, and therefore the comparison is rather qualitative. Our calculated value of 4.98 is consistent with previous work: M.H. Du [14] reported a value of 5.06 for $\overline{\epsilon^\infty}$ and Umari et al. [117] calculated an electronic dielectric permittivity of 5.5 within the PBE approximation to the exchange-correlation functional.

Our results computed for PBE, DFT-D3, and DFT-D3(BJ) parametrizations as well as results found in the literature are reported in table 4.13. They are all consistent with previous work as the maximum difference compared to Ref. [14] is $\sim 2\%$. Moreover, the measured dielectric constant of $\text{CH}_3\text{NH}_3\text{PbI}_3$ at high frequency is 6.5 [118].

ecut [Ha]	50	50	50	18 [14]
ngkpt	4x3x4	4x3x4	4x3x4	1x2x1 (tetra)
	PBE	DFT-D3	DFT-D3(BJ)	PBE
ϵ_a^∞	5.1356	5.2736	5.3547	5.30
ϵ_b^∞	4.5754	4.6947	4.6857	4.62
ϵ_c^∞	5.2151	5.2526	5.3777	5.27
$\overline{\epsilon^\infty}$	4.9754	5.0636	5.1394	5.06

Table 4.13: Calculated electronic dielectric tensor for the orthorhombic phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$. The last column includes results reported by M.H. Du [14].

The static dielectric permittivity tensor $\epsilon(0)$ is obtained by adding the ionic contribution to the electronic dielectric tensor. Its value is given by evaluating the following formula in $\omega = 0$:

$$\epsilon_{\alpha\beta}(\omega) = \epsilon_{\alpha\beta}(\infty) + \frac{4\pi}{\Omega_0} \sum_m \frac{\left(\sum_{\kappa\alpha'} Z_{\kappa,\alpha\alpha'}^* U_{mq=0}^*(\kappa\alpha') \right) \left(\sum_{\kappa'\beta'} Z_{\kappa',\beta\beta'}^* U_{mq=0}(\kappa'\beta') \right)}{\omega_m^2 - \omega^2}$$

ecut [Ha]	50	50	50	18 [14]
ngkpt	4x3x4	4x3x4	4x3x4	1x2x1 (tetra)
	PBE	DFT-D3	DFT-D3(BJ)	PBE
ϵ_a^0	31.9443	21.8667	18.7198	25.40
ϵ_b^0	29.4995	20.8455	17.5148	17.83
ϵ_c^0	62.9124	28.5985	22.8811	21.88
$\bar{\epsilon}^0$	41.4521	23.7702	19.7052	21.70

Table 4.14: Calculated static dielectric tensor for the orthorhombic phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$. The last column includes results reported by M.H. Du [14].

The computed results are given in table 4.14, as well as results found in the literature.

As the experimental value reported by Poglitsch and Weber [51] is 30.5 at 126 K, the calculated static dielectric tensor within the PBE approximation is clearly too high, especially the contribution along the c axis. This overestimation is significantly higher than what can be expected from our density functional approach and the origin of this difference remains poorly understood. However, we can analyze the contribution of the phonon modes. Figure 4.12 shows the calculated frequency-dependent permittivity tensor: ϵ_a (figure 4.12(a)), ϵ_b (figure 4.12(b)), ϵ_c (figure 4.12(c)). The permittivities are represented for the three parametrizations under study. The three components for the PBE parametrization are reported in figure 4.12(d).

Moreover, in table 4.15, the contributions of the different phonon modes to the static dielectric tensor are indicated. For the ϵ_a , the contributions originate from the IR-active B_{3u} modes, while the phonon mode contributions to ϵ_b and ϵ_c come from the IR-active B_{2u} and B_{1u} modes, respectively. The most important contributions to the dielectric screening arise from the rigid-body motion of the PbI_3 network. Along the a axis, modes of symmetry B_{3u} at frequencies 31.4, 35.3, 39.8 cm^{-1} correspond to Pb-I-Pb rocking and the ones at frequencies 49.0 and 65.4 cm^{-1} to Pb-I stretching. Similarly, along the b axis, modes of symmetry B_{2u} at frequencies 27.1 and 31.7 cm^{-1} correspond to Pb-I-Pb rocking, the mode at frequency 42.0 to Pb-I-Pb bending and the modes at frequency 54.7 cm^{-1} to Pb-I stretching. Finally, along the c axis, modes of symmetry B_{1u} at frequencies 20.3 and 26.4 cm^{-1} correspond to Pb-I-Pb rocking and the ones at frequencies 43.7 and 57.3 cm^{-1} to Pb-I-Pb bending and Pb-I stretching, respectively. The contributions of these modes are highlighted in figure 4.12(a), 4.12(b), and 4.12(c).

It is clear that the static dielectric constant is large compared to most of the compound semiconductors with similar band gaps [14]. Moreover, the dielectric screening is dominated by the lattice polarization, rather than electronic one. Actually, the large static dielectric constant is a consequence of the enhanced Born effective charges for Pb which are more than doubled from its nominal ionic charge. The large static dielectric constant gives rise to an effective screening of the impurities and thereby reduces the carrier scattering and trapping. The carrier lifetime and diffusion length in $\text{CH}_3\text{NH}_3\text{PbI}_3$ are therefore increased.

4.2.7 LO-TO splitting

The longitudinal optic (LO) - transverse optic (TO) splitting of phonon modes and the directionality-dependence of the Gamma limit originate from the long-wave-vector electric field caused by the polarization involved by the atomic displacements. By calculating the nonanalytical part of the dynamical matrix (equation 3.106, both TO and LO frequencies can be computed. Table 4.16 is divided in three main parts allowing the study of the LO-TO splitting in each direction. The four first columns include the LO-TO splitting in the z direction induced by IR-active modes of B_{1u} symmetry. The four next columns include the

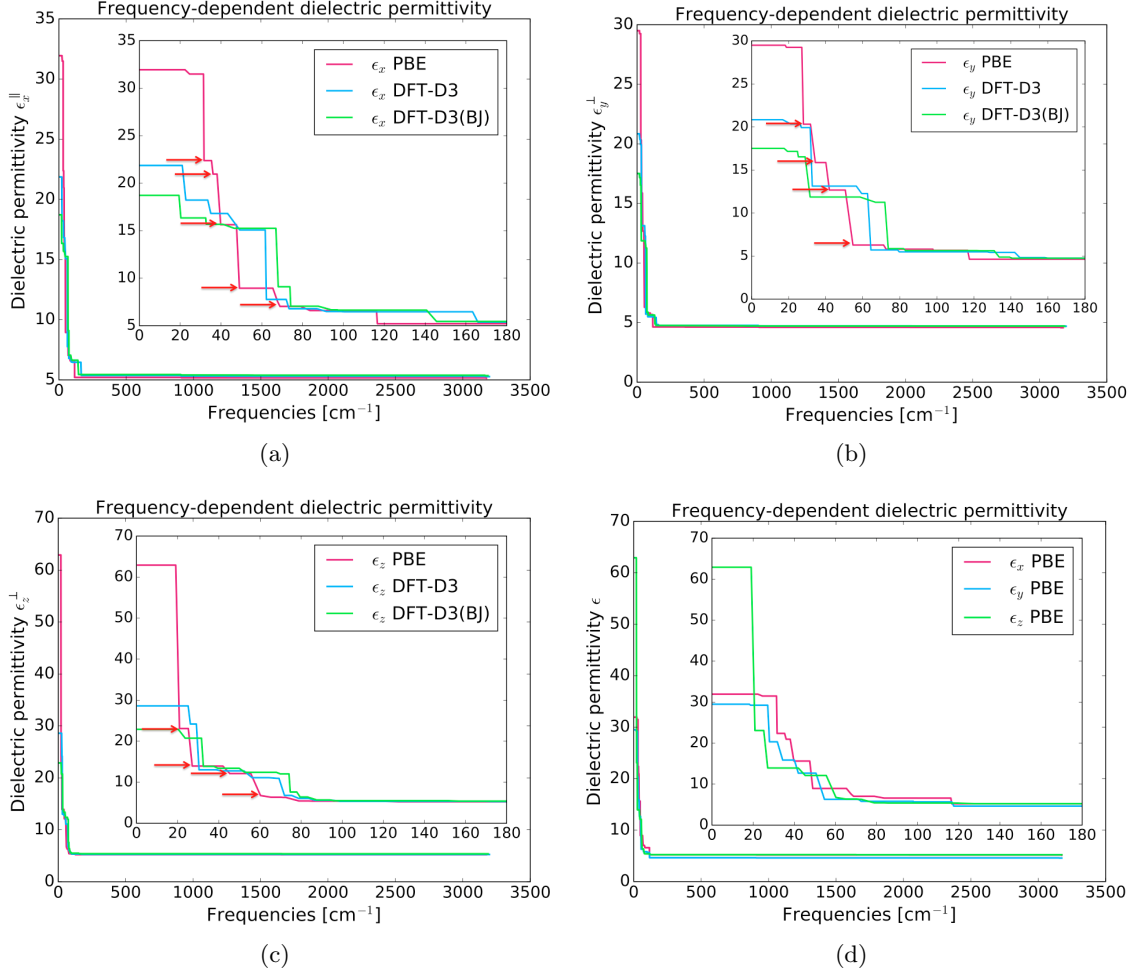


Figure 4.12: Cumulative contribution of the different phonon modes to the dielectric permittivity: (a) Along the a axis, (b) Along the b axis, (c) Along the c axis. Pink lines refer to values computed within the PBE approximation while blue and green lines correspond to the DFT-D3 and DFT-D3(BJ) method, respectively. (d) Frequency-dependent dielectric tensor calculated within the PBE approximation. Red arrows indicate the most important contributions to the static dielectric permittivity.

LO-TO splitting in the y direction induced by IR-active modes of B_{2u} symmetry, and the four last columns include the LO-TO splitting in the x direction induced by IR-active modes of B_{3u} symmetry.

Based on these results, it is possible to assign the IR-activity to some particular modes. Table 4.17 summarizes, for the 13 peaks of figure 4.13, the number of the modes involved in the IR-activity, their frequency, and their symmetry.

The first three first peaks with frequencies $< 100 \text{ cm}^{-1}$ originate from vibrations of the PbI_3 network. The next peak corresponds to the rigid-body motions of the MA cations (figure 4.8(b)). Around $907\text{-}909 \text{ cm}^{-1}$, a high-intensity peak arises from the CH_3NH_3 rocking (figure 4.8(d) and 4.8(e)). Just next to this peak, at 965 cm^{-1} , a smaller one corresponds to C-N stretching (figure 4.8(f)). We then have three peaks at 1255 cm^{-1} , $\sim 1403 \text{ cm}^{-1}$, and $\sim 1450 \text{ cm}^{-1}$ corresponding to CH_3NH_3 rocking (figure 4.8(g)), CH_3 bending (figure 4.8(h)) and NH_3 bending (figure 4.8(j)), respectively. A small feature at 1591 cm^{-1} originates from NH_3 bending (figure 4.8(k)) too. After crossing a gap of almost 1600 cm^{-1} , we find three peaks. The first one at 3119 cm^{-1} has a reasonable intensity and is assigned to a combination

	PBE			DFT-D3			DFT-D3(BJ)		
	$\epsilon^{\parallel}(\omega)$	$\epsilon^{\perp}(\omega)$	$\epsilon^{\perp}(\omega)$	$\epsilon^{\parallel}(\omega)$	$\epsilon^{\perp}(\omega)$	$\epsilon^{\perp}(\omega)$	$\epsilon^{\parallel}(\omega)$	$\epsilon^{\perp}(\omega)$	$\epsilon^{\perp}(\omega)$
ϵ^{∞}	5.14	4.58	5.22	5.27	4.70	5.25	5.35	4.69	5.38
$\Delta\epsilon_1$	0.46	0.25	39.83	3.64	0.48	4.42	2.38	0.35	2.15
$\Delta\epsilon_2$	9.11	8.92	9.14	1.40	0.43	11.16	0.64	0.63	6.87
$\Delta\epsilon_3$	1.42	4.46	0.02	0.01	6.80	0.26	0.03	4.67	0.47
$\Delta\epsilon_4$	5.33	3.19	1.82	1.73	0.87	1.66	0.42	0.61	0.99
$\Delta\epsilon_5$	6.68	6.39	5.36	7.31	6.55	0.16	6.15	5.38	0.38
$\Delta\epsilon_6$	1.42	0.48	0.41	0.98	0.23	4.17	2.05	0.23	4.42
$\Delta\epsilon_7$	0.50	0.14	0.05	0.29	0.06	0.71	0.38	0.01	1.21
$\Delta\epsilon_8$	0.44	1.03	0.86	0.03	0.60	0.49	0.03	0.74	0.72
$\Delta\epsilon_9$	1.38	0.01	0.04	1.08	0.07	0.23	1.19	0.12	0.18
$\Delta\epsilon_{10}$	0.03	0.02	0.16	0.05	0.01	0.07	0.04	0.01	0.10
$\Delta\epsilon_{11}$	0.03	0.03		0.01	0.03	0.01	0.01	0.04	0.01
$\Delta\epsilon_{12}$				0.03	0.02	0.01	0.01	0.03	
$\Delta\epsilon_{13}$							0.01		
$\Delta\epsilon_{14}$							0.03		
ϵ^0	31.94	29.50	62.91	21.87	20.85	28.60	18.72	17.51	22.88

Table 4.15: Electronic and static dielectric tensors for the orthorhombic phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$, computed within the PBE approximation. The contributions of the different phonon modes to the static dielectric tensor are listed.

of N-H (figure 4.8(n)) and C-H stretching (figure 4.8(m)). The two other peaks with the highest intensity both correspond to N-H stretching (figure 4.8(o) and 4.8(p)).

Similarly to the dielectric permittivity tensor, the LO frequencies depend on the oscillator strength tensor, as mentioned in equation 3.107. However, the square of the frequency does not appear in the expression of the LO frequencies, while it divides the oscillator strength in equation 3.103 for the dielectric permittivity. Therefore, even if the high-frequency modes do not contribute consequently to the dielectric constant, their infrared intensity is not negligible and they appear in the IR absorption spectrum.

The same study can be performed for the IR absorption spectrum calculated with the DFT-D3 and DFT-D3(BJ) methods. Results for the LO-TO splitting are shown in table 4.18 and 4.19 for the DFT-D3 and DFT-D3(BJ) method, respectively. The IR absorption spectrum with the contributions of the IR-active modes in the three directions are given in figures 4.14 and 4.15 and the assignment of the vibrational modes with the visible peaks is performed in tables 4.20 and 4.21.

As shown in figure 4.11, the different curves have almost the same shape. At low temperature, the IR absorption peaks are shifted to highest temperature when including the van der Waals corrections. Their intensity is also modified. Moreover, the small feature around 80 cm^{-1} in the pink curve has almost disappeared in the two other curves. Instead, we find a new peak around $130\text{--}150\text{ cm}^{-1}$. This peak originates from rigid-body motions of the CH_3NH_3 cations. In the mid-frequency range, only the intensity of the peaks increase from PBE to DFT-D3 to DFT-D3(BJ) parametrization. Such variations can come from the initial difference in the Born effective charges computed within the three different approximations. Finally, at high frequencies, the peaks are shifted towards the highest frequencies when including the van der Waals interactions, which leads to a better agreement with the experiment [13]. Again, the intensity varies depending on the exchange-correlation functional that we use.

Sym	Modes no.	Freq [cm ⁻¹]	≠ [cm ⁻¹]	Sym	Modes no.	Freq [cm ⁻¹]	≠ [cm ⁻¹]	Sym	Modes no.	Freq [cm ⁻¹]	≠ [cm ⁻¹]
B _{1u}	TO(7)	20.3	4.3	B _{2u}	TO(5)	18.8	0.1	B _{3u}	TO(10)	22.4	0.1
	LO(7)	24.6			LO(5)	18.9			LO(10)	22.5	
B _{1u}	TO(12)	26.4	11.7	B _{2u}	TO(13)	27.1	2.3	B _{3u}	TO(18)	31.4	2.4
	LO(12)	38.1			LO(13)	29.4			LO(18)	33.8	
B _{1u}	TO(23)	36.1	~0	B _{2u}	TO(20)	31.8	3.9	B _{3u}	TO(22)	35.3	0.9
	LO(23)	36.1			LO(20)	35.7			LO(22)	36.2	
B _{1u}	TO(28)	43.7	3.4	B _{2u}	TO(27)	42.0	3.5	B _{3u}	TO(25)	39.8	3.6
	LO(28)	47.1			LO(27)	45.5			LO(25)	43.4	
B _{1u}	TO(36)	57.3	3.0	B _{2u}	TO(34)	54.7	14.6	B _{3u}	TO(31)	49.0	11.6
	LO(36)	60.3			LO(34)	69.3			LO(31)	60.6	
B _{1u}	TO(37)	60.5	9.8	B _{2u}	TO(44)	71.3	16.2	B _{3u}	TO(38)	65.4	1.8
	LO(37)	70.3			LO(44)	87.5			LO(38)	67.2	
B _{1u}	TO(43)	70.6	2.0	B _{2u}	TO(57)	97.9	2.0	B _{3u}	TO(39)	67.7	8.7
	LO(43)	72.6			LO(57)	99.9			LO(39)	76.4	
B _{1u}	TO(45)	75.7	8.0	B _{2u}	TO(66)	117.6	23.7	B _{3u}	TO(46)	79.0	12.5
	LO(45)	83.7			LO(66)	141.3			LO(46)	91.5	
B _{1u}	TO(49)	83.9	22.1	B _{2u}	TO(72)	149.1	~0	B _{3u}	TO(53)	86.5	~0
	LO(49)	106.0			LO(72)	149.1			LO(53)	86.5	
B _{1u}	TO(67)	121.4	6.1	B _{2u}	TO(75)	356.5	0.3	B _{3u}	TO(65)	116.6	27.4
	LO(67)	127.5			LO(75)	356.8			LO(65)	144.0	
B _{1u}	TO(79)	908.0	0.4	B _{2u}	TO(78)	907.9	2.5	B _{3u}	TO(83)	909.3	2.7
	LO(79)	908.4			LO(78)	910.4			LO(83)	912.0	
B _{1u}	TO(86)	964.8	0.4	B _{2u}	TO(90)	1252.1	0.2	B _{3u}	TO(87)	964.8	0.1
	LO(86)	965.2			LO(90)	1252.3			LO(87)	964.9	
B _{1u}	TO(94)	1255.2	~0	B _{2u}	TO(101)	1444.2	0.2	B _{3u}	TO(95)	1255.2	0.4
	LO(94)	1255.2			LO(101)	1444.4			LO(95)	1255.6	
B _{1u}	TO(99)	1403.3	~0	B _{2u}	TO(113)	1572.7	0.1	B _{3u}	TO(98)	1403.2	~0
	LO(99)	1403.3			LO(113)	1572.8			LO(98)	1403.2	
B _{1u}	TO(108)	1446.0	0.1	B _{2u}	TO(131)	3083.4	~0	B _{3u}	TO(102)	1444.5	0.2
	LO(108)	1446.1			LO(131)	3083.4			LO(102)	1444.7	
B _{1u}	TO(111)	1453.0	0.8	B _{2u}	TO(139)	3156.1	9.0	B _{3u}	TO(110)	1448.2	0.4
	LO(111)	1453.8			LO(139)	3165.1			LO(110)	1448.6	
B _{1u}	TO(120)	1592.9	~0					B _{3u}	TO(117)	1591.2	0.1
	LO(120)	1592.9							LO(117)	1591.3	
B _{1u}	TO(123)	2981.9	~0					B _{3u}	TO(124)	2982.0	~0
	LO(123)	2981.9							LO(124)	2982.0	
B _{1u}	TO(125)	3082.8	~0					B _{3u}	TO(129)	3082.9	~0
	LO(125)	3082.8							LO(129)	3082.9	
B _{1u}	TO(136)	3118.9	0.6					B _{3u}	TO(135)	3118.2	0.3
	LO(136)	3119.5							LO(135)	3118.5	
B _{1u}	TO(143)	3173.5	0.8					B _{3u}	TO(142)	3173.5	9.9
	LO(143)	3174.3							LO(142)	3183.4	

Table 4.16: LO-TO splitting of IR-active modes. The four first columns include the LO-TO splitting in the z direction induced by IR-active modes of B_{1u} symmetry. The four next columns include the LO-TO splitting in the y direction induced by IR-active modes of B_{2u} symmetry, and the four last columns include the LO-TO splitting in the x direction induced by IR-active modes of B_{3u} symmetry. The TO and LO frequencies are computed within the PBE approximation.

Peaks no	Modes no	Freq [cm ⁻¹]	Sym	Modes no	Freq [cm ⁻¹]	Sym	Modes no	Freq [cm ⁻¹]	Sym
1	7	20.3	B _{1u}	12	26.4	B _{1u}	18	31.4	B _{3u}
2	31	49.0	B _{3u}	34	54.7	B _{2u}	37	60.5	B _{1u}
3	45	75.7	B _{1u}	46	79.0	B _{3u}	49	83.9	B _{1u}
4	65	116.6	B _{3u}	66	117.6	B _{2u}	67	121.4	B _{1u}
5	78	907.5	B _{2u}	79	908.0	B _{1u}	83	909.3	B _{3u}
6	86	964.8	B _{1u}						
7	95	1255.2	B _{3u}						
8	98	1403.2	B _{3u}	99	1403.3	B _{1u}			
9	110	1448.2	B _{3u}	111	1453.0	B _{1u}			
10	117	1591.2	B _{3u}						
11	136	3118.9	B _{1u}						
12	139	3156.1	B _{2u}						
13	142	3173.5	B _{3u}						

Table 4.17: Parallel between the LO-TO splitting, linked to the Born effective tensor via the oscillator strength tensor and the IR intensity represented in figure 4.13, for the PBE parametrization

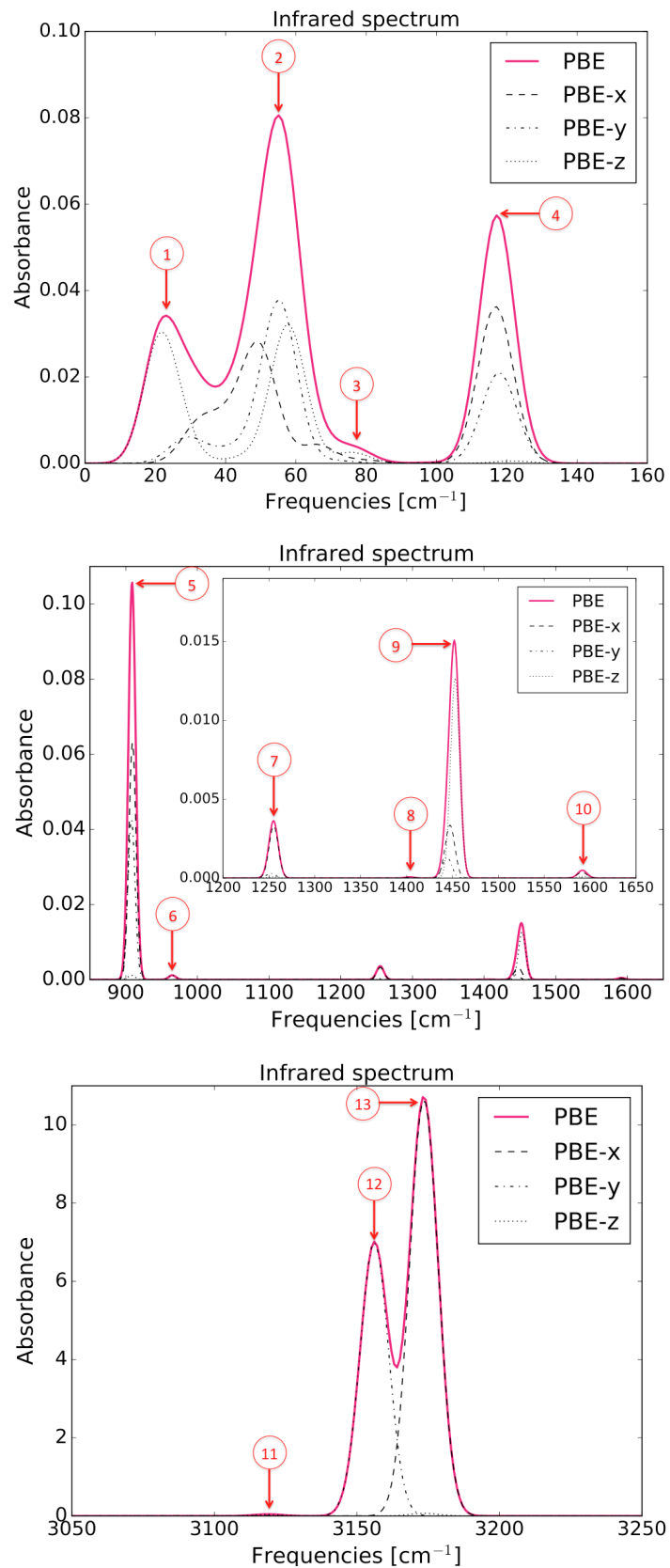


Figure 4.13: IR active peaks highlighted by the LO-TO splitting in each direction, computed within the PBE approximation to the exchange-correlation functional. The pink curve corresponds to the sum of the three contributions.

Sym	Modes no.	Freq [cm ⁻¹]	≠ [cm ⁻¹]	Sym	Modes no.	Freq [cm ⁻¹]	≠ [cm ⁻¹]	Sym	Modes no.	Freq [cm ⁻¹]	≠ [cm ⁻¹]
B _{1u}	TO(9)	25.3	0.9	B _{2u}	TO(5)	21.0	0.2	B _{3u}	TO(6)	22.8	0.3
	LO(9)	26.2			LO(5)	21.2			LO(6)	23.1	
B _{1u}	TO(12)	30.3	3.5	B _{2u}	TO(10)	26.9	0.1	B _{3u}	TO(17)	33.5	1.2
	LO(12)	38.8			LO(10)	27.0			LO(17)	34.7	
B _{1u}	TO(22)	40.2	1.6	B _{2u}	TO(15)	31.6	5.9	B _{3u}	TO(21)	37.7	~0
	LO(22)	41.8			LO(15)	37.5			LO(21)	37.7	
B _{1u}	TO(28)	53.2	3.0	B _{2u}	TO(30)	59.4	0.5	B _{3u}	TO(26)	49.2	1.5
	LO(28)	56.2			LO(30)	59.9			LO(26)	50.7	
B _{1u}	TO(35)	68.3	0.1	B _{2u}	TO(34)	64.4	13.6	B _{3u}	TO(32)	62.2	8.1
	LO(35)	68.4			LO(34)	78.0			LO(32)	70.3	
B _{1u}	TO(37)	70.3	5.1	B _{2u}	TO(41)	78.8	21.7	B _{3u}	TO(38)	71.9	12.8
	LO(37)	75.4			LO(41)	100.5			LO(38)	84.7	
B _{1u}	TO(40)	76.6	5.1	B _{2u}	TO(59)	128.7	0.8	B _{3u}	TO(42)	79.7	~0
	LO(40)	83.7			LO(59)	129.5			LO(42)	79.7	
B _{1u}	TO(45)	85.6	10.3	B _{2u}	TO(63)	144.8	10.4	B _{3u}	TO(46)	87.0	10.8
	LO(45)	95.9			LO(63)	155.2			LO(46)	97.8	
B _{1u}	TO(50)	98.1	19.9	B _{2u}	TO(67)	159.9	5.3	B _{3u}	TO(51)	98.9	3.8
	LO(50)	118.0			LO(67)	165.2			LO(51)	102.7	
B _{1u}	TO(72)	171.0	1.7	B _{2u}	TO(74)	334.8	0.3	B _{3u}	TO(70)	165.8	21.3
	LO(72)	172.7			LO(74)	335.1			LO(70)	187.1	
B _{1u}	TO(81)	905.2	0.4	B _{2u}	TO(78)	904.4	3.3	B _{3u}	TO(83)	906.4	4.2
	LO(81)	905.6			LO(78)	907.7			LO(83)	910.6	
B _{1u}	TO(87)	967.6	0.3	B _{2u}	TO(93)	1250.1	0.1	B _{3u}	TO(86)	967.4	0.2
	LO(87)	967.9			LO(93)	1250.2			LO(86)	967.6	
B _{1u}	TO(94)	1250.1	0.1	B _{2u}	TO(107)	1442.5	0.4	B _{3u}	TO(90)	1249.7	1.1
	LO(94)	1250.2			LO(107)	1442.9			LO(90)	1250.8	
B _{1u}	TO(97)	1403.6	0.1	B _{2u}	TO(113)	1559.9	~0	B _{3u}	TO(100)	1403.7	0.3
	LO(97)	1403.7			LO(113)	1559.9			LO(100)	1404.0	
B _{1u}	TO(103)	1439.6	0.1	B _{2u}	TO(131)	3076.9	~0	B _{3u}	TO(102)	1435.7	1.1
	LO(103)	1439.7			LO(131)	3076.9			LO(102)	1436.8	
B _{1u}	TO(111)	1444.7	1.0	B _{2u}	TO(143)	3190.0	7.9	B _{3u}	TO(105)	1440.6	~0
	LO(111)	1445.7			LO(143)	3197.9			LO(105)	1440.6	
B _{1u}	TO(119)	1584.4	0.1					B _{3u}	TO(117)	1583.4	~0
	LO(119)	1584.5							LO(117)	1583.4	
B _{1u}	TO(124)	2974.1	~0					B _{3u}	TO(123)	2974.0	~0
	LO(124)	2974.1							LO(123)	2974.0	
B _{1u}	TO(125)	3074.4	~0					B _{3u}	TO(127)	3074.4	~0
	LO(125)	3074.4							LO(127)	3074.4	
B _{1u}	TO(135)	3118.8	~0					B _{3u}	TO(133)	3115.1	2.1
	LO(135)	3118.8							LO(133)	3117.2	
B _{1u}	TO(138)	3169.7	1.2					B _{3u}	TO(140)	3171.9	9.0
	LO(138)	3170.9							LO(140)	3180.9	

Table 4.18: LO-TO splitting of IR-active modes. The four first columns include the LO-TO splitting in the z direction induced by IR-active modes of B_{1u} symmetry. The four next columns include the LO-TO splitting in the y direction induced by IR-active modes of B_{2u} symmetry, and the four last columns include the LO-TO splitting in the x direction induced by IR-active modes of B_{3u} symmetry. The TO and LO frequencies are computed in the DFT-D3 framework.

Sym	Modes no.	Freq [cm ⁻¹]	≠ [cm ⁻¹]	Sym	Modes no.	Freq [cm ⁻¹]	≠ [cm ⁻¹]	Sym	Modes no.	Freq [cm ⁻¹]	≠ [cm ⁻¹]
B _{1u}	TO(8)	22.9	1.8	B _{2u}	TO(6)	19.4	0.2	B _{3u}	TO(7)	20.3	1.3
	LO(8)	23.7			LO(6)	19.6			LO(7)	21.6	
B _{1u}	TO(15)	31.6	5.1	B _{2u}	TO(11)	25.2	0.3	B _{3u}	TO(16)	32.5	0.6
	LO(15)	36.7			LO(11)	25.5			LO(16)	33.1	
B _{1u}	TO(22)	38.8	1.6	B _{2u}	TO(14)	31.6	5.1	B _{3u}	TO(21)	37.6	0.1
	LO(22)	40.4			LO(14)	36.7			LO(21)	37.7	
B _{1u}	TO(28)	52.3	1.7	B _{2u}	TO(31)	66.9	0.5	B _{3u}	TO(26)	46.5	0.5
	LO(28)	54.0			LO(31)	67.4			LO(26)	47.0	
B _{1u}	TO(33)	69.6	0.3	B _{2u}	TO(35)	73.8	7.7	B _{3u}	TO(32)	68.0	4.3
	LO(33)	69.9			LO(35)	81.5			LO(32)	72.3	
B _{1u}	TO(37)	74.2	3.7	B _{2u}	TO(44)	82.0	21.4	B _{3u}	TO(36)	74.2	~0
	LO(37)	77.9			LO(44)	103.4			LO(36)	74.2	
B _{1u}	TO(40)	79.3	3.8	B _{2u}	TO(60)	123.2	0.2	B _{3u}	TO(42)	79.8	6.0
	LO(40)	83.1			LO(60)	123.4			LO(42)	85.8	
B _{1u}	TO(45)	84.3	9.7	B _{2u}	TO(63)	133.7	5.6	B _{3u}	TO(46)	87.6	9.0
	LO(45)	94.0			LO(63)	139.3			LO(46)	96.6	
B _{1u}	TO(47)	94.9	25.7	B _{2u}	TO(67)	140.7	14.6	B _{3u}	TO(50)	97.0	8.0
	LO(47)	120.6			LO(67)	155.3			LO(50)	105.0	
B _{1u}	TO(72)	154.0	2.8	B _{2u}	TO(74)	340.7	0.3	B _{3u}	TO(69)	149.1	22.9
	LO(72)	156.8			LO(74)	341.0			LO(69)	172.0	
B _{1u}	TO(83)	905.2	0.3	B _{2u}	TO(77)	901.0	3.4	B _{3u}	TO(84)	906.2	3.2
	LO(83)	905.5			LO(77)	904.4			LO(84)	909.4	
B _{1u}	TO(87)	970.6	0.3	B _{2u}	TO(89)	1251.2	0.2	B _{3u}	TO(86)	970.5	0.1
	LO(87)	970.9			LO(89)	1251.4			LO(86)	970.6	
B _{1u}	TO(95)	1253.5	0.1	B _{2u}	TO(107)	1443.6	0.3	B _{3u}	TO(93)	1253.2	0.8
	LO(95)	1253.6			LO(107)	1443.9			LO(93)	1254.0	
B _{1u}	TO(98)	1401.8	~0	B _{2u}	TO(113)	1565.2	~0	B _{3u}	TO(99)	1402.1	~0
	LO(98)	1401.8			LO(113)	1565.2			LO(99)	1402.1	
B _{1u}	TO(103)	1442.1	0.2	B _{2u}	TO(131)	3087.6	~0	B _{3u}	TO(102)	1438.0	0.8
	LO(103)	1442.3			LO(131)	3087.6			LO(102)	1438.8	
B _{1u}	TO(111)	1445.3	0.7	B _{2u}	TO(143)	3179.3	9.0	B _{3u}	TO(105)	1442.5	0.1
	LO(111)	1446.0			LO(143)	3188.3			LO(105)	1442.6	
B _{1u}	TO(120)	1586.5	0.1					B _{3u}	TO(117)	1585.0	0.1
	LO(120)	1586.6							LO(117)	1585.1	
B _{1u}	TO(124)	2984.3	~0					B _{3u}	TO(123)	2984.2	0.1
	LO(124)	2984.3							LO(123)	2984.3	
B _{1u}	TO(125)	3083.6	~0					B _{3u}	TO(133)	3113.6	1.8
	LO(125)	3083.6							LO(133)	3115.4	
B _{1u}	TO(135)	3117.2	~0					B _{3u}	TO(140)	3165.3	10.2
	LO(135)	3117.2							LO(140)	3175.5	
B _{1u}	TO(138)	3163.2	1.2								
	LO(138)	3164.4									

Table 4.19: LO-TO splitting of IR-active modes. The four first columns include the LO-TO splitting in the z direction induced by IR-active modes of B_{1u} symmetry. The four next columns include the LO-TO splitting in the y direction induced by IR-active modes of B_{2u} symmetry, and the four last columns include the LO-TO splitting in the x direction induced by IR-active modes of B_{3u} symmetry. The TO and LO frequencies are computed in the DFT-D3(BJ) framework.

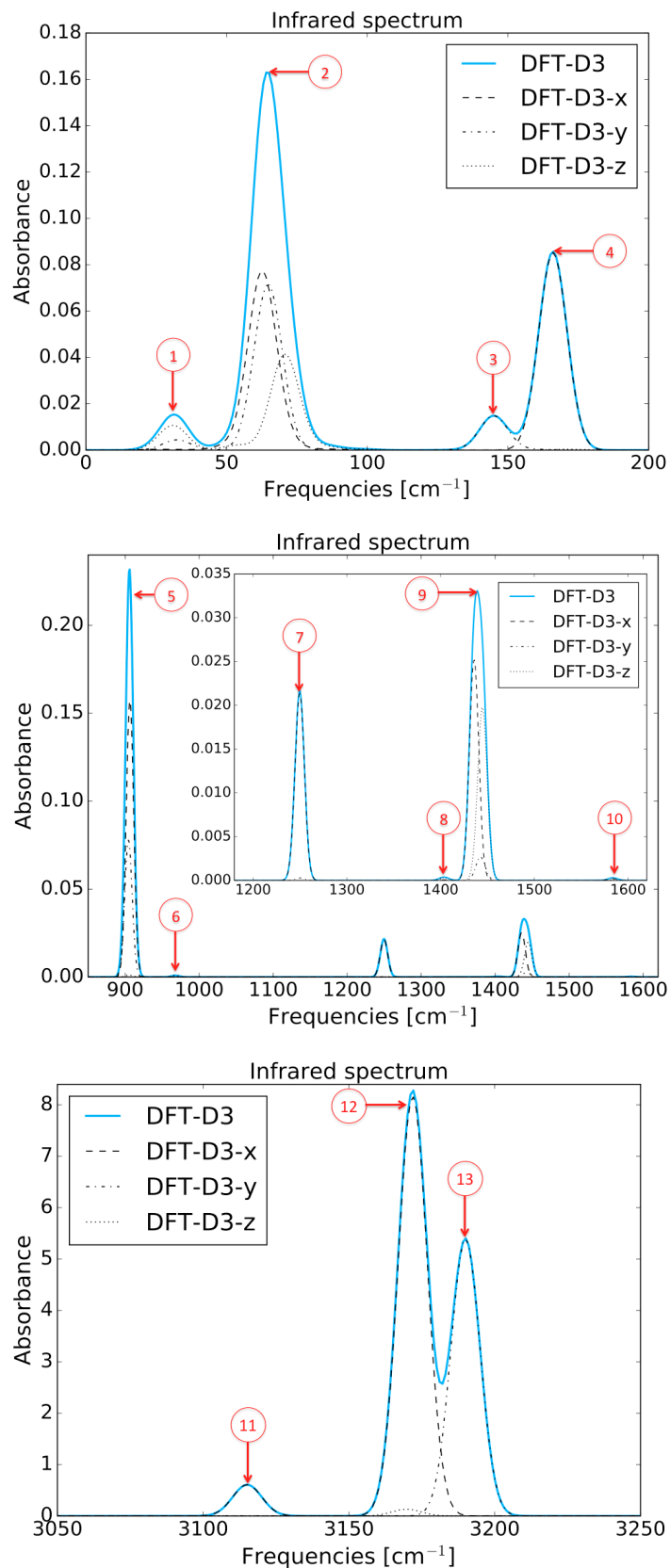


Figure 4.14: IR active peaks highlighted by the LO-TO splitting in each direction, computed within the DFT-D3 method, and hence, including the van der Waals interactions. The blue curve corresponds to the sum of the three contributions.

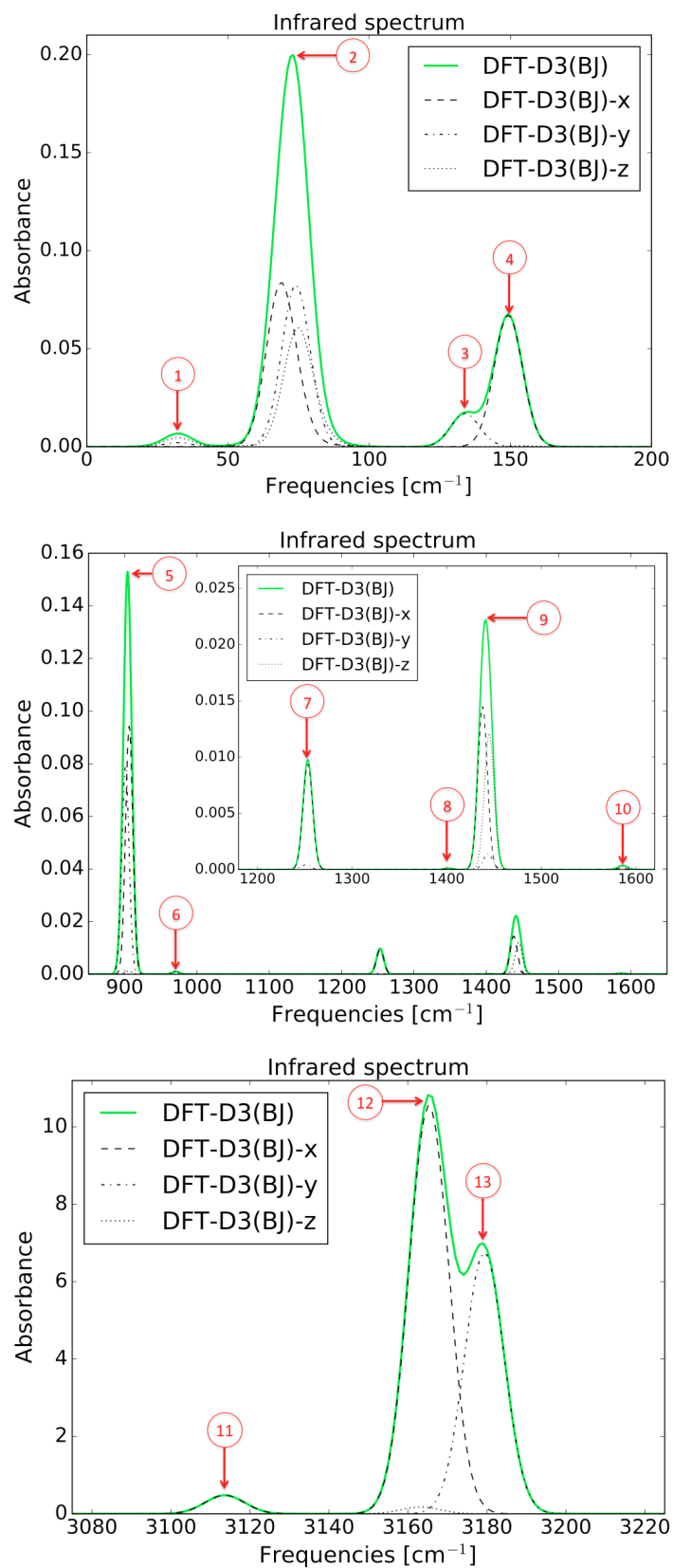


Figure 4.15: IR active peaks highlighted by the LO-TO splitting in each direction, computed within the DFT-D3(BJ) method, and hence, including the van der Waals interactions. The green curve corresponds to the sum of the three contributions.

Peaks no	Modes no	Freq [cm ⁻¹]	Sym	Modes no	Freq [cm ⁻¹]	Sym	Modes no	Freq [cm ⁻¹]	Sym
1	12	30.3	B _{1u}	15	31.6	B _{2u}			
2	32	62.2	B _{3u}	34	64.4	B _{2u}	37	70.3	B _{1u}
	38	71.9	B _{3u}	40	76.6	B _{1u}	41	78.8	B _{2u}
	45	85.6	B _{1u}						
3	63	144.8	B _{2u}						
4	70	165.8	B _{3u}	72	171.0	B _{1u}			
5	78	904.4	B _{2u}	83	906.4	B _{3u}			
6	86	967.4	B _{3u}	87	967.6	B _{1u}			
7	90	1249.7	B _{3u}						
8	97	1403.6	B _{1u}	100	1403.7	B _{3u}			
9	102	1435.7	B _{3u}	111	1444.7	B _{1u}			
10	117	1583.4	B _{3u}	119	1584.4	B _{1u}			
11	133	3115.1	B _{3u}						
12	138	3169.7	B _{1u}	140	3171.9	B _{3u}			
13	143	3190.0	B _{2u}						

Table 4.20: Parallel between the LO-TO splitting, linked to the Born effective tensor via the oscillator strength tensor and the IR intensity represented in figure 4.14, for the DFT-D3 method.

Peaks no	Modes no	Freq [cm ⁻¹]	Sym	Modes no	Freq [cm ⁻¹]	Sym	Modes no	Freq [cm ⁻¹]	Sym
1	14	31.6	B _{2u}	15	31.6	B _{1u}	22	38.8	B _{1u}
2	32	68.0	B _{3u}	35	73.8	B _{2u}	37	74.2	B _{1u}
	40	79.3	B _{1u}	42	79.8	B _{3u}	44	82.0	B _{2u}
3	63	133.7	B _{2u}	67	140.7	B _{2u}			
4	69	149.1	B _{3u}						
5	77	901.0	B _{2u}	84	906.2	B _{3u}			
6	87	970.6	B _{1u}						
7	93	1253.2	B _{3u}						
8	102	1438.0	B _{3u}	107	1443.6	B _{2u}			
9	98	1401.8	B _{1u}	99	1402.1	B _{3u}			
10	120	1586.5	B _{1u}						
11	133	3113.6	B _{3u}						
12	140	3165.3	B _{3u}						
13	143	3179.3	B _{2u}						

Table 4.21: Parallel between the LO-TO splitting, linked to the Born effective tensor via the oscillator strength tensor and the IR intensity represented in figure 4.15, for the DFT-D3(BJ) method.

Chapter 5

Discussion

5.1 Structural and electronic properties

The structural parameters reported in table 4.2 are in good agreement with the experimental data reported by Huang et al. [11] and Baikie et al. [12].

The quasiparticle band gap is one of the most important materials properties for photovoltaic applications. Even if our calculated band gap within the PBE approximation was in good agreement with the experimental value, lots of factors have to be taken into account in order to get a correct description. Among these factors, we find the quasiparticle self-energy, the spin-orbit coupling, the inclusion of semicore electrons, and structural distortions.

The effect of the inclusion of the GW self-energy and spin-orbit coupling effects is shown in figure 5.1.

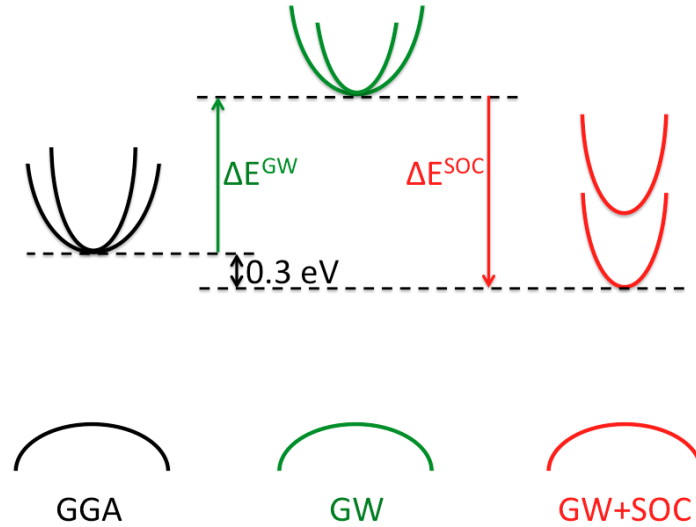


Figure 5.1: Schematic diagram showing the variation of the band gap when including the quasiparticle self-energy ΔE^{GW} and the spin-orbit coupling effects ΔE^{SOC} . Adapted from [8].

Moreover, Weiwei Gao et al. [8] reported a band gap of 1.72 eV calculated with a simple self-consistent scissor-correction approach SS-GW. Figure 5.2 shows the bandstructure of the low-temperature orthorhombic phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$ obtained from DFT+SOC and SS-GW.

Based on these different theories for the computation of the band gap, different values can be found. Moreover, the inclusion of fully-relativistic effects via the spin-orbit coupling

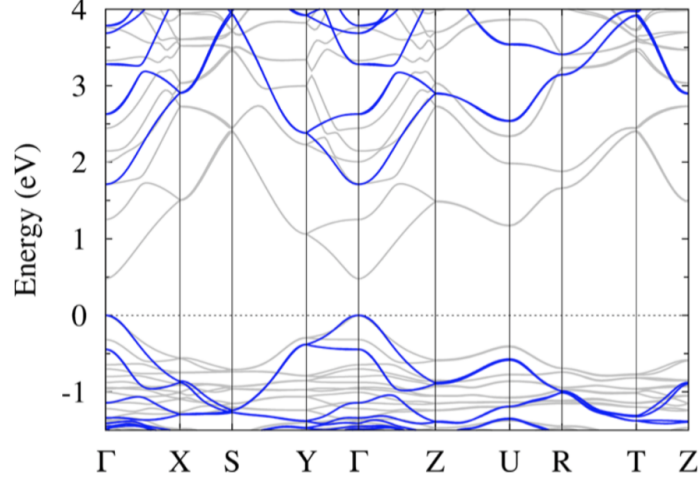


Figure 5.2: Bandstructure of the low-temperature orthorhombic phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$ obtained from DFT+SOC (grey) and SS-GW (blue) on the following path: Γ (0,0,0) - X (0.5,0,0) - S (0.5,0.5,0) - Y (0,0.5,0) - Γ - Z (0,0,0.5) - U (0.5,0,0.5) - R (0.5,0.5,0.5) - T (0,0.5,0.5) - Z [9].

gives rise to a reduction of about 0.9 eV of the initial values. Table 5.1 summarizes the main results found in the literature.

	DFT/LDA	G_0W_0	SS-GW	Experimental [119]
SR	1.50	2.55	2.68	1.62-1.64
FR (SOC)	0.58	1.32	1.79	

Table 5.1: Band gap of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in its low-temperature orthorhombic phase reported for different calculations. SR refers to scalar-relativistic calculations while FR refers to fully-relativistic calculations. All values are calculated for the optimized structure. Adapted from [9].

Another effect influencing the band gap stays in the lattice parameters. Indeed, Marina R. Filip et al. [9] reported a band gap of 1.20 within the G_0W_0 approximation calculated at the experimental parameters, while a band gap of 1.32 is found when considering the optimized lattice parameters.

Besides, our results were computed with pseudopotentials including semicore levels for the lead atoms but not for the iodide atoms. Marina R. Filip et al. [9] reported that the inclusion of semicore states increases the calculated band gap by 0.2 eV. Table 5.2 shows the value of the band gap for different combinations.

	DFT	DFT	DFT	DFT	G_0W_0	G_0W_0	G_0W_0	G_0W_0
	Pb ws	Pb ws	Pb ws	Pb ws	Pb ws	Pb ws	Pb ws	Pb ws
	I ws	I ws	I ws	I ws	I ws	I ws	I ws	I ws
SR	1.43	1.42	1.51	1.50	2.20	2.16	2.61	2.55
FR	0.54	0.52	0.6	0.58	1.08	0.98	1.42	1.32

Table 5.2: Results of scalar relativistic (SR) and fully relativistic (FR) calculations for all combinations of Pb and I pseudopotentials showing the influence of the inclusion of semicore electrons. ws and wos indicate that semicore electrons are respectively included or not in the pseudopotentials. Results are presented for both DFT/LDA and G_0W_0 methods. Adapted from [9].

These results indicate that even if the DFT/LDA results do not change too much, the GW quasiparticle corrections are sensitive to the inclusion of semicore electrons in the valence and, and especially of the I-4d semicore electrons.

It has been shown in a recent study [8] that organic molecules do not directly affect the band gap. However, the presence of MA cations introduces some distortions to the PbI_3^- network which control the overall lattice constants. Therefore, the organic part contributes exclusively to the electronic properties of hybrid organic-inorganic perovskites but the band gap energy is dominated by the inorganic component. Figure 5.3 shows the electronic band structure and partial density of states of the cubic and orthorhombic polymorphs, highlighting the fact that the inclusion of MA cations does not modify consequently the band gap value, as the top of the valence band and the bottom of the conduction band are mainly composed of I-5p and Pb-6p states. The bands due to the MA cations are situated in the middle of the valence band, more than 5 eV lower than the band gap region.

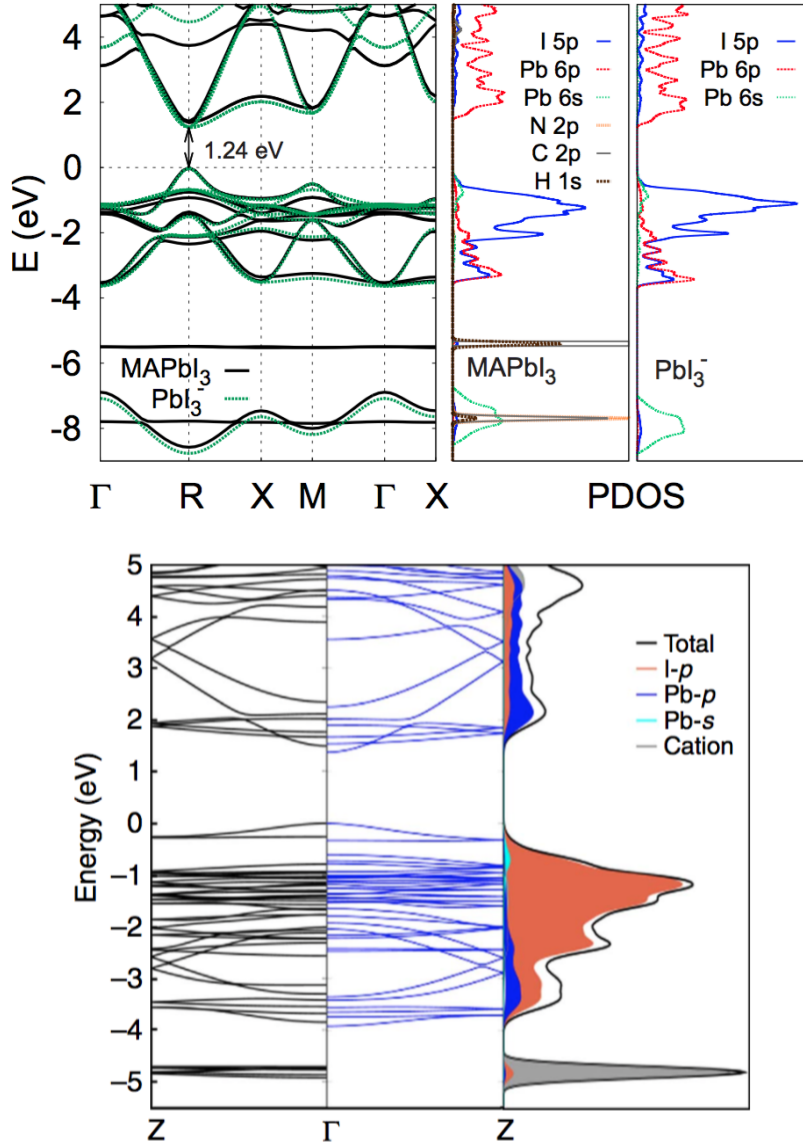


Figure 5.3: DFT scalar relativistic electronic band structure and partial density of states (PDOS) of (a) the cubic [8] and (b) the orthorhombic polymorphs [10] of $\text{CH}_3\text{NH}_3\text{PbI}_3$. Bandstructure are respectively for the PbI_3^- (green dashed curve in (a) and black solid curve in (b)) and the $\text{CH}_3\text{NH}_3\text{PbI}_3$ (black solid curve in (a) and blue solid curve in (b)). The SOC are not included.

Eventually, it can be interesting to study the evolution of the electronic properties when the temperature increases. Such temperature-dependence of the band structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ has been studied by Baikie et al. [12]. The cubic phase has a well-defined direct band gap of 1.3 eV at the $R(1/2, 1/2, 1/2)$ point. The cubic structure transforms into a tetragonal ($I4/mcm$) phase with the tilting of the PbI_6 octahedron when temperature decreases, which moves the band to the $\Gamma(0, 0, 0)$ due to the lowering of the lattice symmetry, and the band gap energy increases to 1.43 eV. It has been shown that the band gap becomes larger when the symmetry decreases and the tilting of octahedral network increases. As the dynamical disorder of methylammonium is removed in the orthorhombic ($Pnma$) phase, CH_3NH_3^+ can be considered in the calculation to show a direct band gap of 1.61 eV at the $\Gamma(0, 0, 0)$. UV-visible spectroscopy has shown that the band gap becomes larger as the symmetry is lowered. Table 5.3 summarizes the energy band gaps of $\text{CH}_3\text{NH}_3\text{PbI}_3$ for the different phases.

	Cubic	Tetragonal	Orthorhombic
Measured [eV]		1.51	
Calculated [eV]	1.3	1.43	1.61

Table 5.3: Energy band gaps of $\text{CH}_3\text{NH}_3\text{PbI}_3$ calculated within the GGA-PBE parametrization by Baikie et al. [12] and measured by UV-visible spectroscopy.

5.2 Vibrational properties

The IR spectrum has been calculated for the PBE, DFT-D3 and DFT-D3(BJ) methods. Moreover, Marina R. Filip et al. [13] reported an experimental IR spectrum measured at 10 K. Figures 5.4, 5.5 and 5.6 respectively show the assignment of our calculated IR peaks and the experimental ones. The best agreement is obtained in the mid-frequency range of the spectrum in the three cases. In the high-frequency region of the spectrum, the larger deviation between theory and experiment is of $\sim 50 \text{ cm}^{-1}$ in the three cases. The inclusion of van der Waals interactions gives rise to a shift of the peaks to higher frequencies. Finally, for the low-frequency range of the spectrum, while there are four prominent peaks and two small features in the measured spectrum, our calculated spectrum (figure 5.4) only shows three prominent peaks at 20 cm^{-1} , 59 cm^{-1} , and 120 cm^{-1} , a hump between 70 and 100 cm^{-1} and a small feature around 100 cm^{-1} . The presence of this small feature can be confirmed by the LO-TO splitting arising around 100 cm^{-1} in the y direction with a B_{2u} symmetry mode, mentioned in table 4.16.

This work focused on the low-temperature orthorhombic phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$. However, a recent study [13] has shown that most of the peaks in the IR spectrum of the orthorhombic phase remain distinguishable in the room-temperature tetragonal phase, while the other peaks merge into broad structures at high temperature.

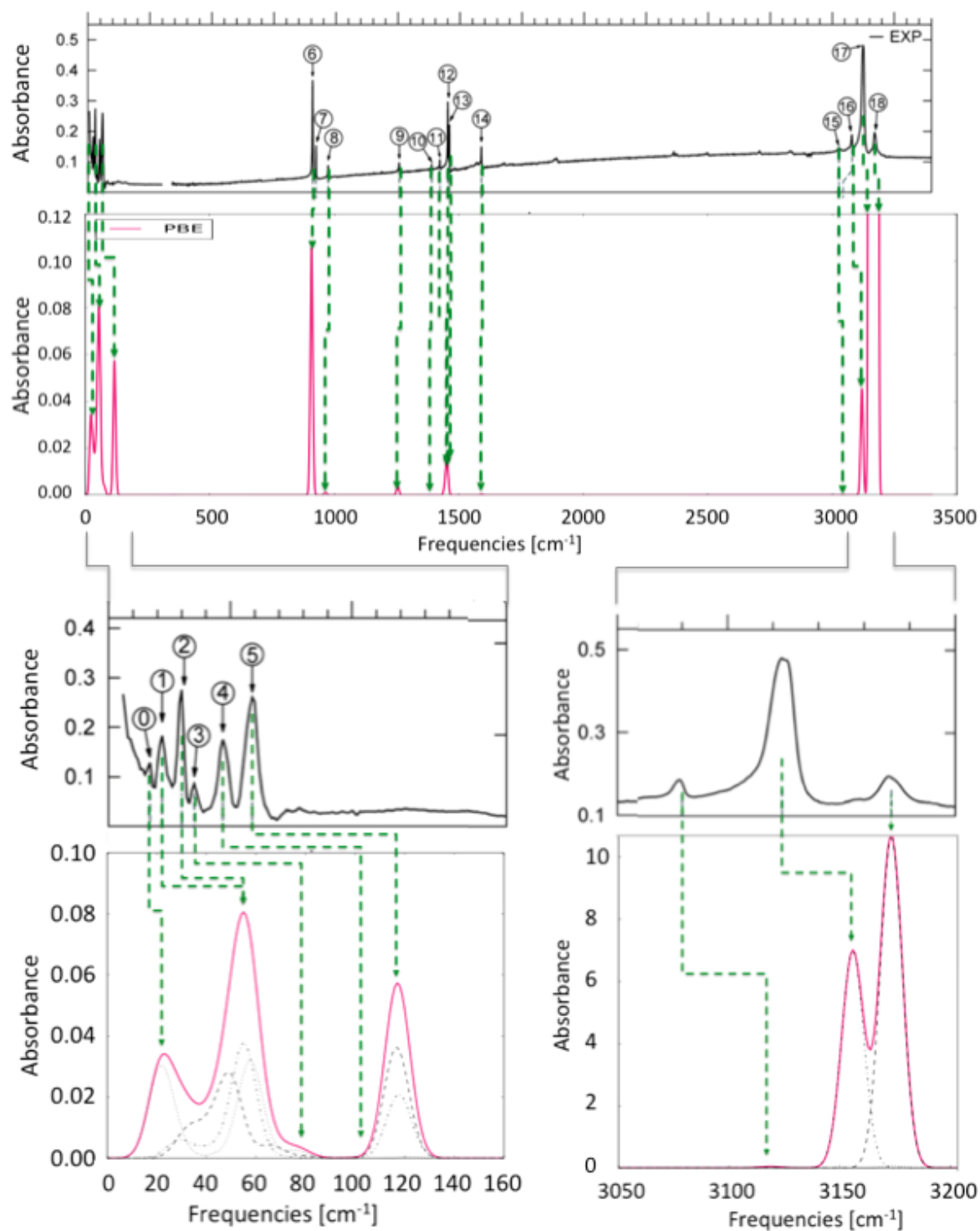


Figure 5.4: Assignment of the IR peaks of our calculated IR spectrum computed within the PBE approximation, with the experimental spectrum measured at 10 K reported in Ref. [13].

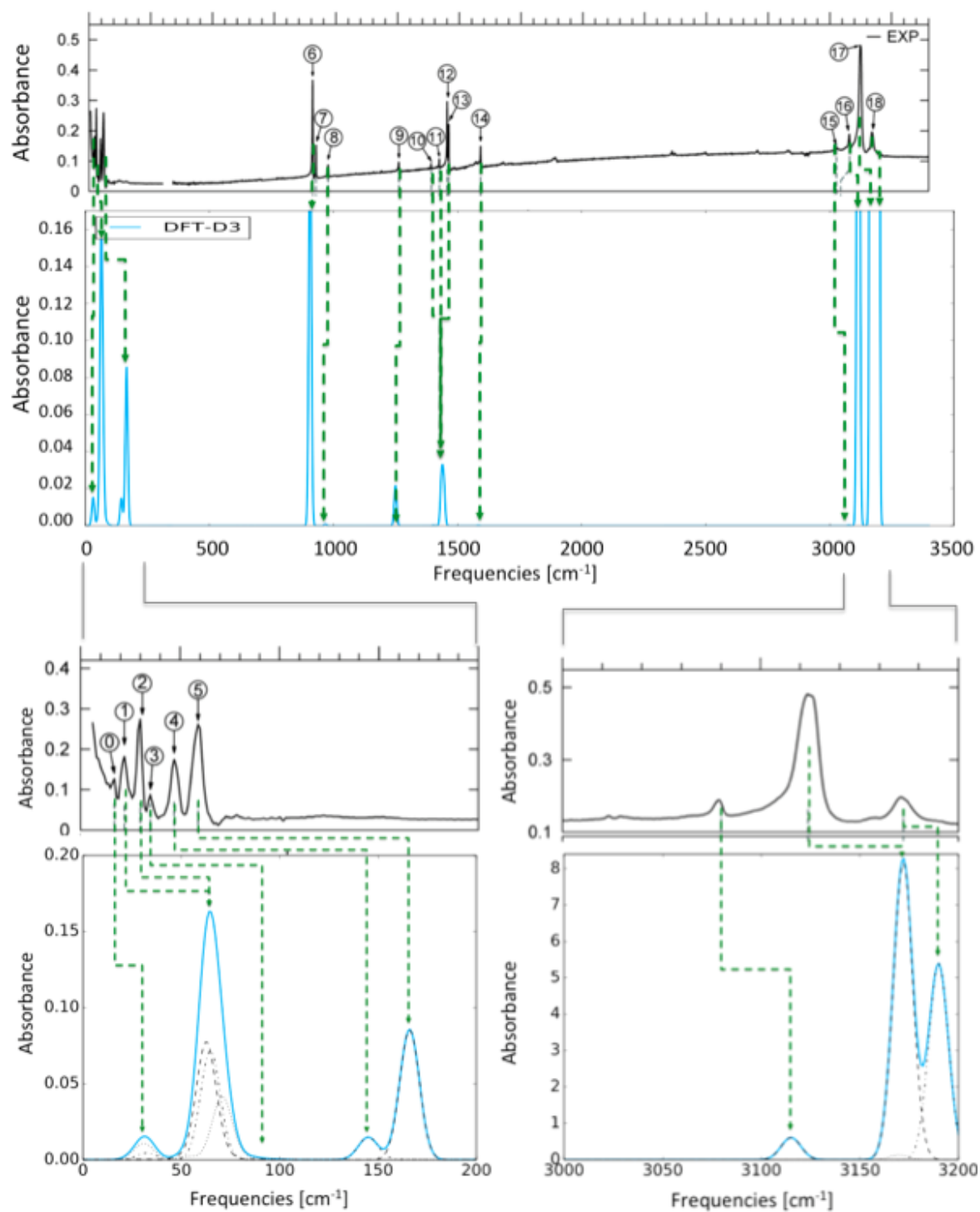


Figure 5.5: Assignment of the IR peaks of our calculated IR spectrum computed with the DFT-D3 method, with the experimental spectrum measured at 10 K reported in Ref. [13].

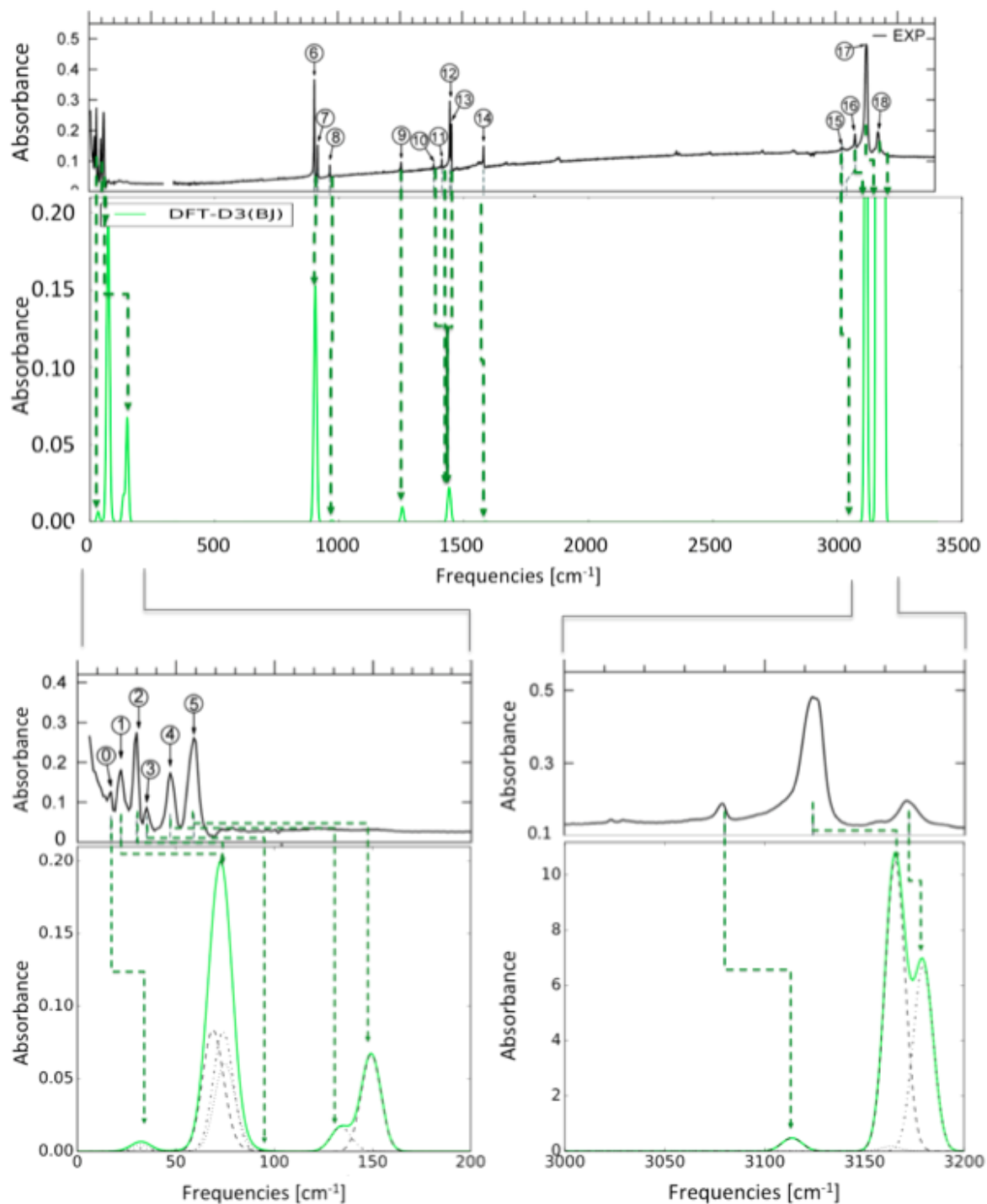


Figure 5.6: Assignment of the IR peaks of our calculated IR spectrum computed with the DFT-D3(BJ) approximation, with the experimental spectrum measured at 10 K reported in Ref. [13].

Chapter 6

Conclusions and prospects

Throughout this work, different properties of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite material have been studied. Structural, electronic and vibrational properties have been numerically calculated thanks to *ab initio* simulations using the DFT and DFPT as implemented by ABINIT in order to understand the exceptionally good carrier transport properties of the material. Simulations were performed for the low-temperature phase because the configuration of the CH_3NH_3^+ cations is well-defined in the orthorhombic phase, while the angular disorder increases with the temperature.

In order to get a better interpretation and comparison with experimental results mentioned in the literature, the spin-orbit coupling and the van der Waals corrections have been included and modeled.

The lattice parameters and structural configuration is quite well described by the PBE approximation to the exchange-correlation functional. Moreover, the inclusion of van der Waals interactions enhance these parameters. On the contrary, the spin-orbit coupling does not have any consequent influence on the structural parameters of the crystal.

The quasiparticle band gap is one of the most important materials properties for photovoltaic applications. The fundamental band gap has been found to be direct and located at the zone center (Gamma). Its value varies from 1.815 eV to 1.667 eV when it is calculated with the PBE approximation or the DFT-D3(BJ) method, respectively. These values are closed to the measured optical gap of 1.61 eV. However, the inclusion of spin-orbit interactions leads to a gap of about 1 eV smaller than the experimental value. Different effects have to be taken into account in order to get a good and physical approximation of the band gap. Some effects and their influence have been discussed.

Vibrational properties have also been studied. The 144 normal modes of vibration have been determined and a factor group analysis has been used to characterize the infrared and Raman activities of each modes. The phonon frequencies can be divided into three well-distinct regions: a low-frequency region from 0 to 150 cm^{-1} , a mid-frequency region from 355 to 1600 cm^{-1} , and a high-frequency region from 2980 to 3200 cm^{-1} .

Our calculated IR spectrum can be partitioned into three distinct regions, depending on the atomic vibrations responsible for the IR activity: at high frequencies, we find the internal vibrations of the MA cations, while at lower frequencies, the cation translations and the internal vibrations of the PbI_3 network, including the Pb-I stretching and Pb-I-Pb bending modes, dominate. Qualitatively, our IR spectrum is in good agreement with the experimental one proposed by Marina R. Filip et al. [13]. Thanks to a comparison with the measured spectrum, we succeeded in assigning the different peaks of our calculated IR spectrum. However, some discrepancies are still present at low frequencies, even after the

inclusion of van der Waals interactions.

Finally, different properties have been studied such as the Born effective charges, the optical and static dielectric constants, and the LO-TO splitting. The large Born effective charges and the resulting large static dielectric permittivity provide an effective screening for impurities and enhance the transport properties of the material.

We hope that the present work will stimulate further studies on the structural, electronic and vibrational properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and related organometal halide perovskites.

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