

# Chapter 1

## Introduction to NV centers and their common usage

The aim of this first chapter is to introduce the tools and concepts required for the next chapters. We will start

### 1.1 The NV center as a physical object

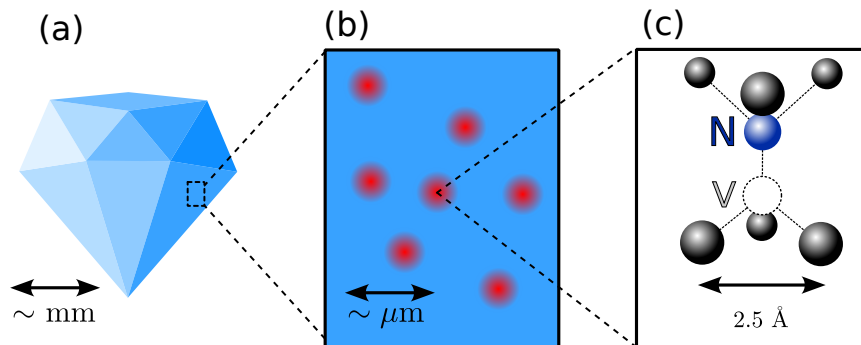


Figure 1.1: From the diamond to the NV center. a) Drawing of a bulk diamond. We consider a diamond to be “bulk” if it is bigger than a few  $100 \mu\text{m}$ . b) Drawing representing a fluorescence microscopy image of a diamond surface. The red fluorescent spots symbolize NV centers. c) Zoom-in on the crystalline structure of an NV center. Block dots represent carbon atoms

Refaire ce paragraphe te foutre le summary après la description de la figure. Et bien parler du NV- et du charge state We will start this chapter by discussing the physical aspect of the NV center, and of its host material, the diamond. We will cover some of the basic properties of diamond and of its most common defects before addressing the creation process of both diamonds and NV centers.

Fig. 1.1 illustrates the various scales to consider in this study: we start with a diamond which for lab purposes is generally no bigger than a few mm. If we zoom-in on the surface of some diamonds, we can find bright fluorescent spots corresponding to particular crystalline defects. Standard confocal microscopy is limited in its resolution to the  $\sim \mu\text{m}$  range, but if we could zoom-in even further we would see the structure of the defect, illustrated here with the crystalline structure of an NV center.

### 1.1.1 Diamond overview

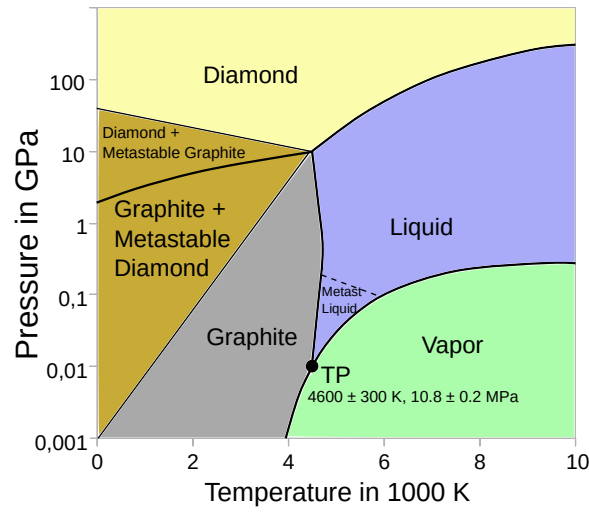


Figure 1.2: Pressure-temperature phase diagram of elemental carbon. From wikipedia, adapted from [1, 2].

Diamond is a remarkable material in many aspects, it is famous for having the highest hardness and thermal conductivity of any natural material, and for its high optical refractive index and optical dispersion which makes it an extremely valuable crystal in jewelry.

Diamond is also famous for being extremely rare in nature, even though its only constituent, carbon, is one of the most abundant element on the Earth surface. The reason is that diamond is not the most stable phase of carbon under atmospheric pressure and temperature. This honor goes to the graphite which is found abundantly in coal.

Fig. 1.2 shows the PT phase diagram of elemental carbon. We can see that diamond becomes the thermodynamically stable phase only for pressure above a few GPa,  $10^4$  times higher than atmospheric pressure. Even though diamond is unstable under ambient conditions, the extremely high energy activation needed to break the  $\text{sp}^3$  bond between two carbon atoms means that the kinematics of the  $C_{\text{diamond}} \rightarrow C_{\text{graphite}}$  transition is

almost completely frozen. In many ways diamonds are more stable than graphite under ambient condition due to their relative chemical inertness.

Where the thermodynamic equilibrium really matters is for the crystallization process. The higher pressure needed to reach the diamond-stable region can only be found naturally deep under the earth crust, typically between 150 and 240 km below sea level [3], which explain their rarity. It also explains why, despite many previous efforts, diamonds were synthetically produced for the first time only in 1953 [4], more than 50 years after the first synthetic sapphires. To this day, artificial diamond synthesis remains an active field of research [5, 6].

Diamonds, either natural or artificial, are used in the lab and in industry for their extreme sturdiness, with applications ranging from abrasive to diamond anvil cells [7]. More recently, diamonds have been the object of optics and electronics applications. For both of these fields however, the focus is no longer solely on the diamond but also on the defects found inside it.

### 1.1.2 Point defects in diamond

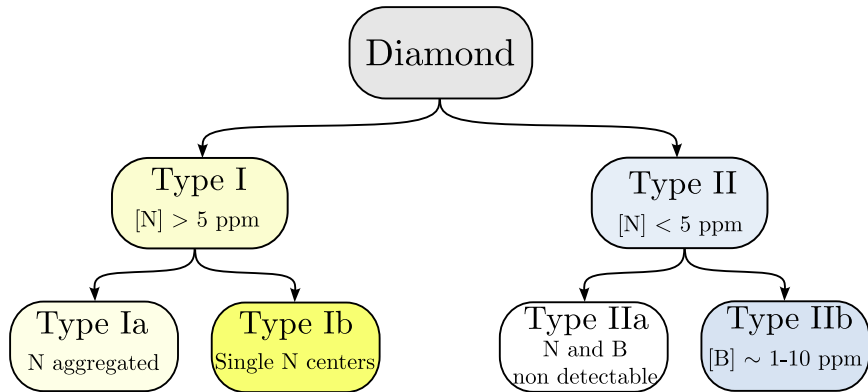


Figure 1.3: Traditional classification of diamonds, based on [3]

Diamond in its intrinsic form is an insulator with a bandgap of  $\sim 5.47$  eV and is transparent from far infrared to deep UV. As any crystal however, diamond is prone to defects. We will concentrate here on 0D point-like defects and omit structural defects such as dislocations, even though those too can affect the optical properties of the diamond [8].

Point-like defects can be constituted by the absence of a carbon atom (“vacancies”), an interstitial defect between two carbon atoms or the substitution of a carbon atom with another atom. These impurities result in unpaired electron or holes localized around the impurity site. This localization causes discrete energy levels for the holes or the electrons, some of which will lie inside the diamond bandgap and will impact the crystal optical and electrical properties.

Defects with electronic transitions in the optical range are called “colored centers” as they are responsible for the coloring of the gems. H, He, Li, B, N, O, Ne, P, Si, As, Ti, Cr, Ni, Co, Zn, Zr, Ag, W, Xe and Tl are known to form colored centers when introduced in diamond [5, 9], and each of these elements can form several defects. Nitrogen alone can form more than 50 different colored centers [10, 11].

Nitrogen, and to a lesser extent boron, are the most commonly found extrinsic elements in natural diamond. The traditional classification of diamond is presented in Fig. 1.3. It is based on the N and B concentration, with a threshold of a few ppm (part per million) for each species as this was the smaller amount easily detectable through IR absorption. Type Ia diamonds contain clustered N defects such as the B-center which is the  $N_4V$  defect. In contrast, type Ib diamond mostly contains C-center which are single substitutional  $N_s$  defects, also referred to as P1 centers in the spin community. Type IIb diamond contains B impurities which give them a blueish-grey color, and type IIa diamond contains no detectable impurities via IR absorption [11].

Nitrogen-vacancy centers are a rare occurrence in both natural diamonds and untreated synthetic diamonds, but we will see later that the much more common  $N_s$  defects can be converted in NV centers. When working with NV centers, the starting crystal is therefore often a type Ib if one wants to work with ensemble, or a type IIa if one wants to work with single NV centers.

The boron defects are mainly studied in the context of p-doped diamond semi-conductor: a concentration of  $[B] \approx 1000$  ppm is needed to achieve a significant overlap between the impurity sites, which turns the diamond into a semi-metal [12]. Other defects of interest, generally not present naturally but introduced voluntarily, include P and S defects to create n-doped diamond [13] (still an active field of research), as well as group IV-vacancy defects ( $SiV$ ,  $GeV$ ,  $SnV$ ,  $PbV$ ) for quantum optics application [14].

The NV center however remains by far the most studied defect in diamond due to its unique spin properties which will be explained below.

### 1.1.3 Creation of synthetic diamond for optics and electronics applications

We will now focus on the creation process of the diamonds. Almost all diamonds used in optics or electronics experiments today are synthetic, due to the higher control of the growth process required for these applications. There are two main competing technologies for the growth of large ( $\mu m \sim mm$ ) single crystal diamonds: High pressure high temperature growth (HPHT) and chemical vapor deposition growth (CVD). Both of these processes have their own specificities which we will detail below.

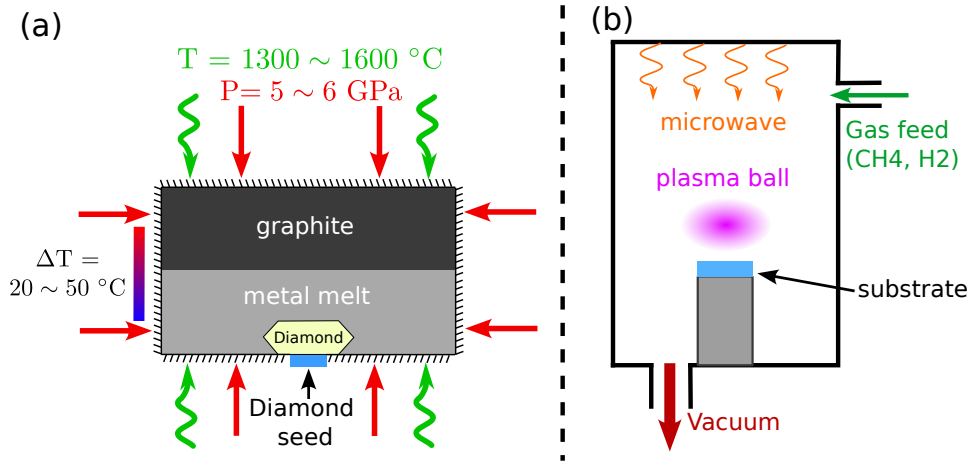


Figure 1.4: Schematics of HPHT (a) and CVD (b) growth process as detailed in main text

### HPHT growth

HPHT was the first commercially viable process for synthetic diamonds, starting from the 1950s [4, 15]. The basic idea of HPHT synthesis is to reconstruct an environment where diamond is the thermodynamically stable phase of carbon, similarly to the growth process of natural diamond below the earth crust.

Fig. 1.4-a) illustrates the apparatus of HPHT synthesis: a carbon source (graphite) and a solvent metal composed of transition metals (Fe, Ni, Co typically [16]) are put under 5 ~ 6 GPa pressure in a press and heated to temperatures  $\geq 1300$  °C. A diamond crystal seed is put in the metal catalyst and a temperature gradient insures that the carbon migrates from the graphite to the diamond.

The first synthesis of HPHT diamonds were all of type Ib due to unwanted nitrogen pollution in the metal melt. The first HPHT type IIa diamonds were produced in the late 90s by adding other elements to the metal melt (Ti, Al, Zr) which would react preferentially with nitrogen and prevent its incorporation in the diamond [17, 18].

### CVD growth

CVD growth for diamond was first demonstrated convincingly in the 80s [19–21]. Unlike HPHT, CVD operates in a regime where diamond is not the thermodynamically stable phase. It relies therefore heavily on catalysts to stabilize the diamond phase versus the graphite one.

The main catalyst used is atomic hydrogen, which can both create the free radicals required to form the  $C - C$  diamond bonds, and which etches  $sp^2$  bonds (graphite) faster than it does  $sp^3$  bonds (diamond) [22]. Hydrogen

is by far the most abundant element in the gas phase: the precursor gases used for the growth are typically  $\text{CH}_4$  and  $\text{H}_2$  in proportions of 1 – 5% and 95 – 99% respectively [6].

Fig. 1.4-b) illustrates the apparatus of a microwave plasma reactor: it consists in a modified vacuum chamber which acts as a microwave resonator. The microwave creates a plasma ball from the precursor gases with a temperature  $T_{\text{plasma}} \geq 3000^\circ\text{C}$  [11], enough to dissociate the  $\text{H}_2$  gas in atomic hydrogen [23]. The plasma acts as the carbon source for the diamond growing on top of the substrate, and as the catalyst to favor the diamond phase. The substrate is kept at a temperature  $700 \sim 1100^\circ\text{C}$  during the growth.

Other sources can be used to create the high temperature required for atomic hydrogen, such as a tungsten hot filament [24], electrical discharge (arcjet) [25] or even an oxygen-acetylene combustion flame [26].

For a good CVD reactor, the main sources of extrinsic impurities the diamond comes from the source gasses [23]. The commercial availability of source gases containing less than  $\sim$  ppm impurities made possible the growth of high purity type IIa CVD diamonds [27–29].

Both HPHT and CVD processes can produce diamonds of high quality for quantum optics or electronics application, each with their pros and cons. HPHT offers better scalability for thick crystals ( $\sim$  mm) and allows the incorporation of heavy atoms (Ge [30], Sn [31]) which can be hard to incorporate from a gas phase. CVD on the other hand allows more versatility in the control of the impurities introduced in the crystal, including an isotopic control on both the impurities and the carbon itself. A particular advantage of CVD growth is the possibility of  $\delta$ -doping where a specific defect is grown only within a thin layer of the crystal, as low as 5 nm [32–34].

#### 1.1.4 Optimizing NV center formation

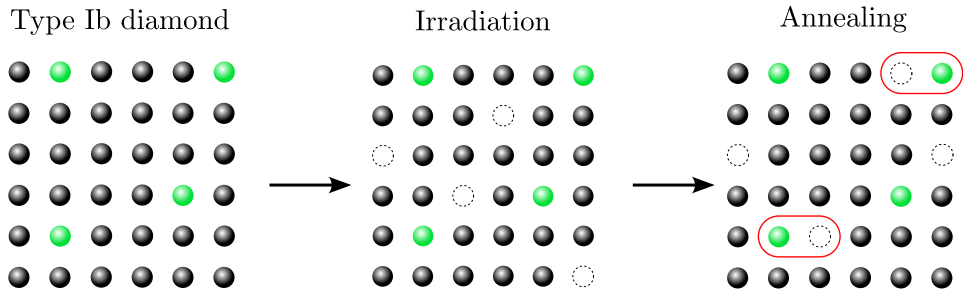


Figure 1.5: Illustration of the formation of NV centers. Black dots represents carbon atoms and green dots nitrogen atoms

NV centers are a relatively rare impurity in untreated diamonds. In CVD diamond for instance, the proportion of nitrogen atoms forming an

NV center in an untreated crystal is at best of 2 – 3% [35] and sometimes much less. While this ratio can sometimes be enough to work with single NV centers, applications such as sensing that require dense ensemble need a higher conversion rate. We will discuss here the usual techniques used to improve the formation of NV centers.

Fig. 1.5 illustrates the steps needed to maximize the number of NV centers in the crystal while keeping a relatively high crystalline purity.

The first step to create NV centers is to get individual substitutional N atoms in the crystal ( $N_s$ , C-centers or P1 centers depending on the literature). This can be achieved either *in situ* by introducing (voluntarily or not) nitrogen in the crystal during the growth process [29, 36], or *ex situ* by implanting  $N^+$  ions with ion implantation techniques [37, 38]. Because this present work focuses on dense NV ensembles, we will consider the simplest case where the starting crystal is a type-Ib diamond due to the presence of nitrogen during the growth. A starting concentration  $[N_s] = 10 \sim 300$  ppm is typical for type Ib HPHT diamonds [6].

The second step is to create monovacancies in the crystal lattice. This step might be optional for crystals which already contain a large number of monovacancies, but CVD crystals in particular can have less vacancies that they have substitutional nitrogen atoms [39]. The general technique to create monovacancy is to bombard the sample with high energy particle in order to knock out carbon atoms from the crystal. Several high energy particle have been used to create vacancies, such as protons, electrons, ions, neutrons and even gamma rays [40–42]. The most common irradiation source for bulk diamond however is electron irradiation (e-beam) [43], thanks to their ability to penetrate the crystal and to create vacancies uniformly.

The final step is to migrate the vacancies next to the nitrogen atoms. The activation energy required to move vacancy is of  $\sim 2.3$  eV which corresponds to temperatures of  $600 \sim 700^\circ\text{C}$  [44, 45]. The most common method to move the vacancies is therefore to anneal the crystal at a temperature  $800 \sim 1200^\circ\text{C}$  for a few hours [46]. NV centers anneal out at temperature of  $1400 \sim 1500^\circ\text{C}$  [9, 47] which explains why the vacancies tend to stick to the nitrogen atoms during the annealing phase.

The final  $N_s$  to NV conversion rate can be as high as  $\sim 50\%$  [35, 48], although this ratio tend to decrease for higher  $[N_s]$  concentrations. Most sample studied in this manuscript had a concentration  $[NV] = 1 - 10$  ppm

### 1.1.5 Controlling the NV center charge state

The charge state of the NV center is of crucial importance for NV applications. Only the negatively charged  $NV^-$  center shows the specific spin properties that will be detailed below, but the NV center can exist under three charge states in the diamond:  $NV^-$ ,  $NV^0$  and  $NV^+$ . The presence of  $NV^+$  is only marginal in standard diamonds [49, 50] and we will focus here

solely on the  $NV^-$  and  $NV^0$  charge state.

The charge state of the NV centers depends not only on the growth process of the crystal, but also on the usage made of the sample. In particular, illumination in the optical range can promote electrons in the conduction band or holes in the valence band and modify the charge state of the NV center.

On the material side, the crystal has to remain electrically neutral which means that at least as many charge donors need to be present as there are  $NV^-$  centers. For nitrogen-rich samples, the donors are mostly  $N^+$  centers, which imposes a limit on the maximum conversion rate of N to NV in order to keep a high  $[NV^-]/[NV^0]$  ratio. The possibility to introduce other donors, such as phosphorus, has been studied [51] but remains impractical so far [52].

On the experimental side, it has been shown that the ionization of  $NV^-$  to  $NV^0$  and the reverse process depend on the intensity and wavelength of the laser used for illumination [53]. It was found that the optimal wavelength to preserve the  $NV^-$  charge state was 510 – 540 nm. The most common wavelength used with NV centers is 532 nm (green) due to the historical importance of Nd:YAG lasers. On the other hand, it is possible to semi-permanently ionize the  $NV^-$  into  $NV^0$  when using a red excitation, which has been used to create an optical memory [54].

For samples in high excess of  $[N_s]$  such as type Ib HPHT diamonds, the question of the charge state of the NV center is of relatively low importance as the  $NV^-$  state is the predominant one. For sample with a lower  $[N_s]$  content and a higher  $[NV]/[N_s]$  ratio however, one must be more careful with the optical intensity and wavelength used as the concentration of  $NV^0$  can reach 50% of the total NV concentration [48]

## 1.2 The $NV^-$ center optical and spin properties

We will now focus on the magnetic and optical properties of the  $NV^-$  center. This section will cover...

### 1.2.1 NV center molecular orbitals

We will first cover the molecular aspect of the NV defect in diamond and the energy levels of the defect predicted from group theory and ab initio computations.

Fig. 1.6-a) illustrates the  $sp^3$  orbitals of the carbons and nitrogen atoms neighboring the vacancy, as well as the 5 electrons occupying dangling bonds from these atoms and a sixth electron captured to form the negatively charged  $NV^-$  state.

Fig. 1.6-b) shows the predicted molecular orbitals of the NV centers, initially computed as linear combination of the  $sp^3$  orbitals respecting the  $C_{3v}$  symmetry of the defect [55]. This model has since been confirmed by



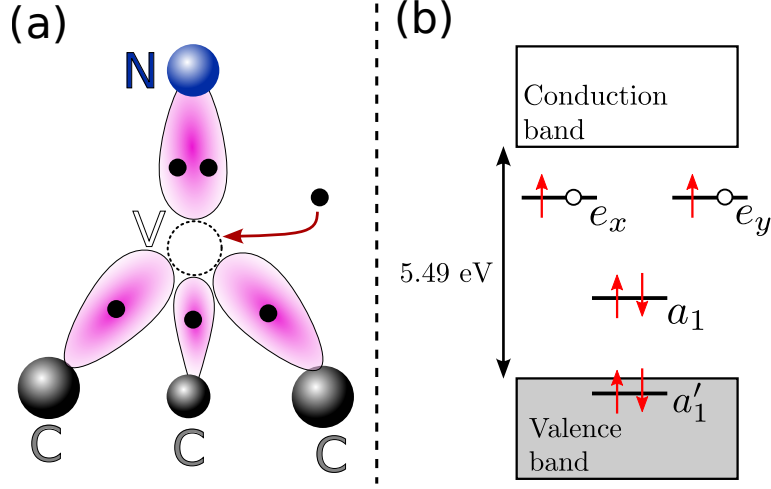


Figure 1.6: (a) Representation of the nitrogen and carbon orbitals surrounding the vacancy of an NV center. Each black dot represents an electron. A sixth electron is required to form the negatively charged NV<sup>-</sup> state. (b) Molecular orbitals of the NV center predicted from the  $C_{3v}$  symmetry of the defect. The electron occupation of the NV<sup>-</sup> ground state is represented by red arrows.

ab initio computation and experimental observations [56]. In particular ab initio computations have shown that the molecular orbitals of the NV center are mostly localized on the nearest neighbors of the vacancy [57]. Ab initio computation has also determined that the  $a'_1$  lies in the valence band and is therefore often ignored.

The electron occupations shown in Fig. 1.6-b) corresponds to the electronic ground state of the NV<sup>-</sup> charge state.

In the remaining part of this manuscript, we will only consider the negatively charged NV<sup>-</sup> state, unless specified otherwise. We will therefore omit the “-” and simply refer to the negatively charged state as “NV”.

### 1.2.2 Optical properties of the NV center

Thanks to the discrete electronic transitions inside the diamond band gap, the NV center is fluorescent: it can absorb light from 450 – 630 nm and re-emits light in the 630 – 800 nm band.

Fig. 1.7 explains the mechanisms of the NV center optical activity. Fig. 1.7-a) illustrates the electronic ground state  $^3A_2$  and first excited state  $^3E$ , where 1 electron from the  $a_1$  molecular orbital is promoted to the  $e$  level. Both of these electron occupations have two unpaired electrons, meaning that they can exist either in a spin triplet state ( $S = 1$ ) or a spin

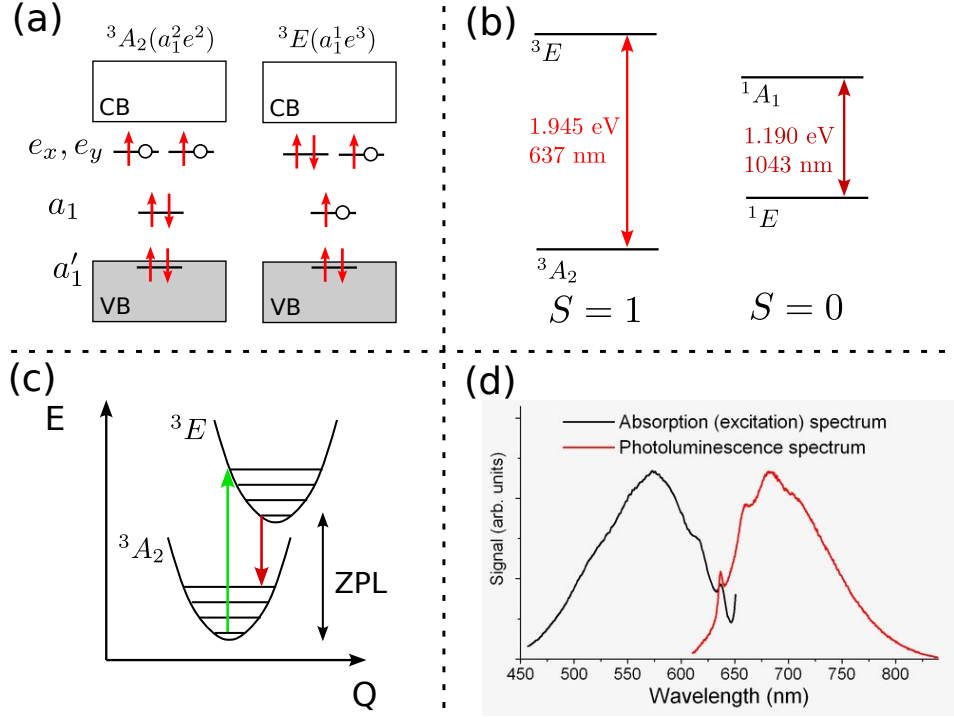


Figure 1.7: Optical properties of the NV center. (a) Electron occupation of the molecular orbitals for the electronic ground state  ${}^3A_2$  and the first excited state  ${}^3E$ . (b) Diagram of the main optical transition between the two spin triplet states and of the IR transition between the two singlet states. The value of the transition corresponds to the ZPL and are taken from [56]. (c) Representation of the vibronic structure for the  ${}^3A_2$  and  ${}^3E$  states under the Franck-Condon approximation. The graph axes are the energy of the states  $E$  and configuration coordinate  $q$ . The green and red arrow represents non-resonant (Stokes or anti-Stokes) absorption and emission. (d) Emission and absorption spectrum of the NV center main transition at 300 K, from PL and PLE measurements respectively. Taken from Wikipedia

singlet state ( $S = 0$ )<sup>1</sup>.

Fig. 1.7-b) shows the zero phonon line (ZPL) for the main transition of the triplet ( ${}^3A_2$  and  ${}^3E$ ) and singlet ( ${}^1E$  and  ${}^1A_1$ ) states. It should be noted that due to an inter system crossing between the  ${}^1E$  and  ${}^3A_2$  levels, excitation or absorption of the singlet transition is only possible with a conjoint excitation of the triplet states. By default, we refer to the NV center photoluminescence (PL) as the emission between the two triplet states.

Fig. 1.7-c) illustrates the vibronic structure of the  ${}^3A_2$  and  ${}^3E$  states

<sup>1</sup>The two singlet states  ${}^1E$  and  ${}^1A_1$  represented in Fig. 1.7-b) are both of configuration  $a_1^2 e^2$  where the two  $e$  electrons are either in a the same  $e$  orbital, or in an antisymmetric superposition of the two  $e$  orbitals [58].

under the Franck-Condon approximation [59]. The emission and absorption of light associated with the triplet transition can be accompanied by the emission or absorption of an optical phonon. Because the lifetime of the optical phonons is very short, the absorption or emission of light almost always start from the fundamental state of the  $^3A_2$  and  $^3E$  level, which explains why the absorption of light can only be done for energies above the ZPL, and the emission for energies below the ZPL (Stokes process).

Finally Fig. 1.7-d) shows the absorption and emission spectrum of NV centers at 300 K. A weak zero-phonon-line is visible at 637 nm, with large phonon sidebands in emission and absorption.

Compared to similar solid state photon sources (other color centers, quantum dots, dye molecules...), the NV center offer several advantages: thanks to the  $\sim 11$  ns lifetime of the excited state and close to 1 quantum efficiency [60], they are very bright. With proper nanophotonics engineering (solid immersion lenses or diamond waveguide) the PL collected from a single NV center can reach a few  $10^6$  photons/s [61]. The NV center is also extremely photostable under green excitation, and does not show any photobleaching [62]. There are however drawbacks in using NV centers for photonics applications, the main one being that  $\leq 4\%$  of the photons emitted by the NV centers are in the ZPL (Debye Waller factor), even at cryogenic temperature [63]. This limits the potential of NV centers for quantum communication protocols that rely on a deterministic photon source [14].

### 1.2.3 Spin properties of the NV center electronic ground state

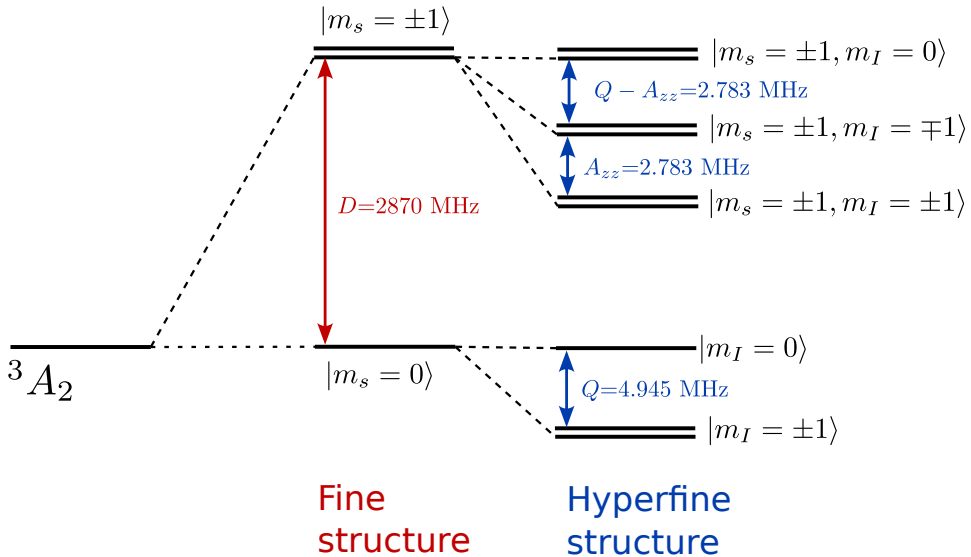


Figure 1.8: tata

For most intent and purposes the hyper-fine structure of the NV center can be ignored, either 1 raie or ensemble.

”particularly long electron and nuclear spin coherence times compared to other solid-state defect center” (Quantum nanophotonics in diamond)

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