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Hydrogen-Related Optical Centers in Natural Diamond: An Update

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Many absorptions in the infrared (IR) and UV-visible range in natural diamond have been related to the presence of hydrogen. The 3107 cm^{-1} system is the most important system in the infrared range, and is related to hydrogen strongly linked to carbon and weakly linked to nitrogen. When the intensity of the 3107 cm^{-1} absorption is greater than that of the intrinsic band at about 2450 cm^{-1}, the diamond is called hydrogen rich (H-rich), and may exhibit specific optical properties; it is typically formed by cuboid growth. In total, about 90 sharp lines or absorption systems have been at least tentatively related to hydrogen in the infrared range (see Table 1); many of them have been documented very recently. Six groups of H-containing diamonds can be defined to help categorize such materials. Three families of color may be found for H-rich diamonds: the "brown to grayish-yellow to green" family, the "gray to blue to violet" family, and the "chameleon" family. The structure at the atomic level of the defects responsible for the component absorptions is still unknown. There seems to be no direct relationship between IR-active centers and visible centers. Furthermore, it is likely that not all the hydrogen is optically active, and the quantification of hydrogen concentration on the basis of optical absorption intensity remains a challenge.

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1. Introduction

Amongst all chemical impurities incorporated during the growth of natural diamond, hydrogen is probably the most important after nitrogen. It is typically identified through its infrared signature, although not all hydrogen present in natural diamond may necessarily be infrared active. The presence of hydrogen affects many physical properties: color, luminescence, growth morphology and the incorporation of other impurities such as nickel.(1) The mode and amount of hydrogen incorporation gives insight into natural diamond growth conditions. Hydrogen is commonly incorporated in CVD-grown diamond,(2) and can passivate boron acceptors in doped synthetic diamonds or otherwise influence the electronic properties of such diamonds.(3,4) Yet, its incorporation in this man-made material is often different from that in natural diamond. This article focuses on the optical centers in natural diamond from the ultraviolet (UV) to the IR range, mostly based on a review of published data, with some input based on the authors' experiences.

Most of the data presented here were acquired using thousands of small faceted gems borrowed from diamond traders, at 4 cm^{-1} resolution, for ease and speed of acquisition, and most stones used for this study are no longer available. Therefore, only peak positions and relative intensities are discussed, not width, because the resolution used is probably insufficient to obtain the true shape of the peaks. Similarly no reliable absolute absorbance data can be deduced from the peak height, because the vast majority of samples do not have parallel windows. These conditions explain why some of the research suggested in the text was not undertaken on the many samples examined.

We will first present a brief history of important discoveries and general concepts, then we will offer a tentative classification of hydrogen-containing diamonds. The various systems and lines that have been at least tentatively attributed to hydrogen-related (H-related, for short) defects are then presented. As much as possible, we have tried to provide the infrared and UV-visible absorption spectra of the same diamonds as shown in the illustrations.

2. History of Research on Hydrogen in Diamond

Hydrogen in diamond was discovered in the late 1950s concomitantly by two laboratories. In 1959, Charette observed, by infrared spectroscopy, a group of sharp lines related to an unknown impurity in diamond, absorptions he called the "1405 cm^{-1} group" (absorptions at 1405, 2787, 3107, 3154, 3237 and 4495 cm^{-1}).(5) The first evidence of hydrogen (H_2) in diamond was found the same year by mass spectrometry of gases escaping from some near-flawless gem diamond crystals.(6) Afterwards, although this destructive method was used several times,(7–9) nondestructive spectroscopic methods were preferred.

The sharp absorptions at 3107 and 1405 cm^{-1}, observed in the infrared absorption of virtually all type Ia diamonds, were then attributed to the presence of hydrogen,(10–13) namely, to the stretching and bending modes of a N-H or C-H vibration bond.(12)

In 1977, chemical analysis using an ion beam (IBSCA) demonstrated that the concentration of hydrogen in natural diamond could reach 1000 atomic ppm,(14) and many confirmations of this followed.(15–17) This hydrogen content takes into account all forms of hydrogen in diamond, whether it is optically active or not. Some attempts have been made to correlate the intensity of the 3107 cm^{-1} absorption peak with the hydrogen concentration using nuclear methods (elastic recoil detection analysis).(18,19)

Hydrogen is involved in a number of defects,(20–26) but the presence of nitrogen seems to be a prerequisite for hydrogen incorporation. Although hydrogen has been detected in very low concentrations in some very rare type IIa natural diamonds,(14,27) it has never been detected in natural, untreated type IIb diamond.(20) In contrast, hydrogen is detected in almost all type Ia diamonds, although sometimes in very small amounts. Also, hydrogen is present in particularly high concentrations in some diamonds with high nitrogen contents.(20,24,28)

Synthetic diamond, in which one can control the isotopic composition of carbon and nitrogen, was used to determine whether the 1405–3107 cm^{-1} system is due to a C-H bond.(20,27,28) It was found by comparison with known vibration frequencies and the force constant that the observed values best fit the vinylidene group, $>C=CH_2$.(20) Recent theoretical calculations have shown that the defect most adequate to induce a vibration at 3107 cm^{-1} is a hydrogen atom located near the bond center between N and C,(29,30) which, once formed, is very stable. This theoretical study also indicates that the shift of peak position with the nitrogen isotope would be very small. This is historically the first satisfactory explanation of the experimental observation that there is no measurable shift. Further details on the 3107 cm^{-1} system are provided later.

The term "hydrogen-rich," or for short, "H-rich," refers to diamonds with an unusually high IR-active hydrogen content and often specific, unusual gemological properties, *e.g.*, specific coloration. This concept was defined by Fritsch and coworkers(23,31) for type Ia diamonds with the intensity of the 3107 cm^{-1} absorption higher than that of the intrinsic band of diamond at 2450 cm^{-1}. These authors distinguished three color families (each with a specific UV-visible absorption spectrum), namely, the "brown to grayish-yellow" family, the "gray to blue to violet" family and the "chameleon" family. White diamond is also H-rich. Hainschwang *et al.* recently discovered what could be called type Ib H-rich diamonds.(26) Such stones exhibit a large amount of presumably H-related features, the strongest being at 2972 cm^{-1}.

Finally, shortly after the definition of the cuboid growth mode in diamond,(32) it was noticed that H-related defects tend to be associated with cuboid growth.(22,25,33) Specifically, there seems to be a systematic association of the H-rich material and the cuboid mode of growth,(31) whether in purely cuboid crystals or only in the cuboid sectors of diamonds obtained by various types of mixed growth. If there is mixed growth, there is often color zoning, with the cuboid sector bearing the H-related color. Also, a wider variety of H-related defects can be observed in cuboid sectors than in adjacent octahedral sectors (Fig. 1).(25) It is, however, not known if the high hydrogen content in the geological medium causes the diamond growth to switch to the cuboid mode or if the cuboid growth occurs for another reason and preferentially incorporates hydrogen. The selective study of growth sectors in mixed-habit diamonds has lead to the observation that the formation of platelets is somewhat quenched in cuboid growth sectors (Fig. 1). Thus, it has been proposed that hydrogen could quench nitrogen aggregation.(25,33)

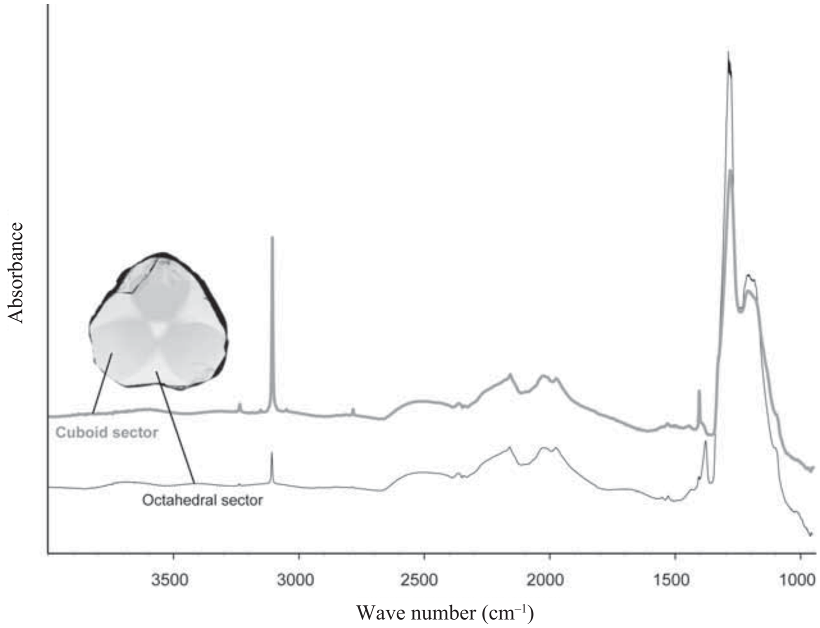

Fig. 1. In mixed-habit, asteriated diamonds, H-related infrared peaks are more intense in cuboid growth sectors that in octahedral ones. Modified from Rondeau *et al*.(25)

Alternately, when there is more nitrogen in the octahedral sectors than in the cuboid sectors, the formation of platelets is simply more probable in octahedral sectors, and the platelet peak is naturally weaker in cuboid sectors.(34)

H-related absorptions are also found in fibrous growth (often confused with cuboid growth when in the form of fibrous cubes). Infrared spectroscopy has recently been helpful for the identification of these growth modes.(35)

The yellowish-green fluorescence of cuboid diamonds has been proposed to be related to the presence of nickel impurities,(24,36) which are better integrated in cuboid diamond than in octahedral diamond.(1) It is unclear whether hydrogen could play a role in the strong phosphorescence observed for (often H-rich) chameleon diamonds.(37)

Recently, some yellow-green to green diamonds from Argyle, Australia, were proven to show properties very close to those of the "brown to grayish yellow family" (see §3.1), so the family name was extended to the "brown to grayish-yellow to green" family.(38)

3. Infrared Signature of Hydrogen in Natural Diamond

We propose here a practical classification useful for grouping the infrared spectra of H-containing diamonds as a whole, that is, as a mixture of features. This is followed by a detailed study of the most important spectral features themselves, whether they are systems or isolated lines. The term *system* refers here to a series of absorptions that are always observed together in the same proportions, and hence are probably induced by a single defect. Table 1 presents all the infrared absorption lines documented so far, and indicates the reference where, to our knowledge, it was first described.

Table 1
H-related infrared absorption lines and the reference in which they were first described. All these absorptions are uniquely observed in hydrogen-containing diamonds, thus they are proposed to all be H-related.

Absorptions (cm^{-1})	References	Comment / Initial attribution
1384	(26)	H in type Ib
1396	(26)	H in type Ib
1401	(26)	H in type Ib
1405	(5)	C-H, 3107 cm^{-1} system
1410	(26)	H in type Ib
1432	(26)	H in type Ib
1461	(26)	H in type Ib
2722	(38)	
2741	(26)	H in type Ib
2750	(38)	
2784–6	(26)	H in type Ib
2786, « 2787 »	(5)	C-H, 3107 cm^{-1} system
2798	(26)	H in type Ib
2812	(25)	
2852	(26)	H in type Ib
2859	(38)	
2869	(26)	H in type Ib
2877	(26)	H in type Ib
2911	(26)	H in type Ib
2932	(26)	H in type Ib
2941	(26)	H in type Ib
2944	(38)	
2949	(26)	H in type Ib
2965	(26)	H in type Ib
2972	(26)	H in type Ib
2982	(40)	3055–2982 cm^{-1} system
2984	(26)	H in type Ib
2994	(26)	H in type Ib
3006	(38)	
3013	(26)	H in type Ib

Absorptions (cm^{-1})	References	Comment / Initial attribution
3026	(26)	H in type Ib
3030	(38)	
3032	(26)	H in type Ib
3041	(26)	H in type Ib
3050, « 3052 »	(10)	3050–3155 cm^{-1} system
3054	(26)	H in type Ib
3055	(40)	3055–2982 cm^{-1} system
3069	(38)	
3072	(26)	H in type Ib
3079, « 3081 »	(10)	
3083	(26)	H in type Ib
3086	(38)	
3093	(22)	
3095	(10)	
3098	(20)	
3107	(5)	C-H, 3107 cm^{-1} system
3122, « 3124 »	(22, 10)	
3133	(20)	
3144, « 3146 »	(20, 10)	
3155, « 3154 »	(5)	3050–3155 cm^{-1} system
3156	(26)	H in type Ib
3162	(38)	
3172	(22)	
3182	(26)	H in type Ib
3189	(22)	
3195	(26)	H in type Ib
3197	(38)	
3208	(38)	
3211	(26)	H in type Ib
3214	(38)	
3236, « 3237 »	(5)	C-H, 3236 cm^{-1} system
3252	(26)	H in type Ib
3255, « 3258 »	(10)	
3262	(38)	
3267	(26)	H in type Ib
3275	(10)	
3286	(38)	
3310, « 3309 »	(10)	
3343	(20)	N-H in type Ib
3354	(38)	
3372	(20)	N-H in type Ib

Absorptions (cm^{-1})	References	Comment / Initial attribution
3394	(20)	N-H in type Ib
3525	(38)	
4167, « 4169 »	(21)	C-H, 3107 cm^{-1} system
4224	(38)	
4240	(38)	
4412	(38)	
4419	(26)	H in type Ib
4431	(26)	H in type Ib
4440	(38)	
4453	(38)	
4464	(38)	
4471	(26)	H in type Ib
4496, « 4499 »	(5, 21)	C-H, 3107 cm^{-1} system
4522	(38)	
4532	(38)	
4535	(26)	H in type Ib
4546	(38)	
4572	(38)	
4588	(38)	
4592	(26)	H in type Ib
4622	(26)	H in type Ib
4630	(38)	
4668	(38)	
4700	(26)	H in type Ib
4703	(38)	C-H, 3236 cm^{-1} system
4722	(38)	
5068	(26)	H in type Ib
5555	(23)	C-H, 3107 cm^{-1} system
5570	(38)	
5626	(38)	
5880	(23)	C-H, 3107 cm^{-1} system
6070	(23)	C-H, 3107 cm^{-1} system
6214	(69)	
6474	(38)	

3.1 *Classification of infrared spectra based on groups of diamond*

The infrared spectra of hydrogen-containing diamonds can be roughly split into 6 groups.

1. Near-colorless type Ia diamonds

   In these stones, the H-related features are always weak and practically limited to the 3107 system. The presence of H-related features is often associated with short episodes of cuboid growth interspersed with the "normal" octahedral growth, as seen by cathodoluminescence, for example. Such crystals are very commonly encountered. As a matter of fact, a type Ia diamond with no hydrogen is a rarity, at least at 4 cm^{-1} resolution.

2. Yellow to brown to green diamonds, plus white to gray diamonds colored by inclusions (scattering effect)

   This group exhibits a relatively large range of infrared spectra,(23) but there is usually less infrared-active hydrogen and nitrogen than in the diamonds of the third group, and usually, the nitrogen is also in a less advanced state of aggregation (Fig. 2).

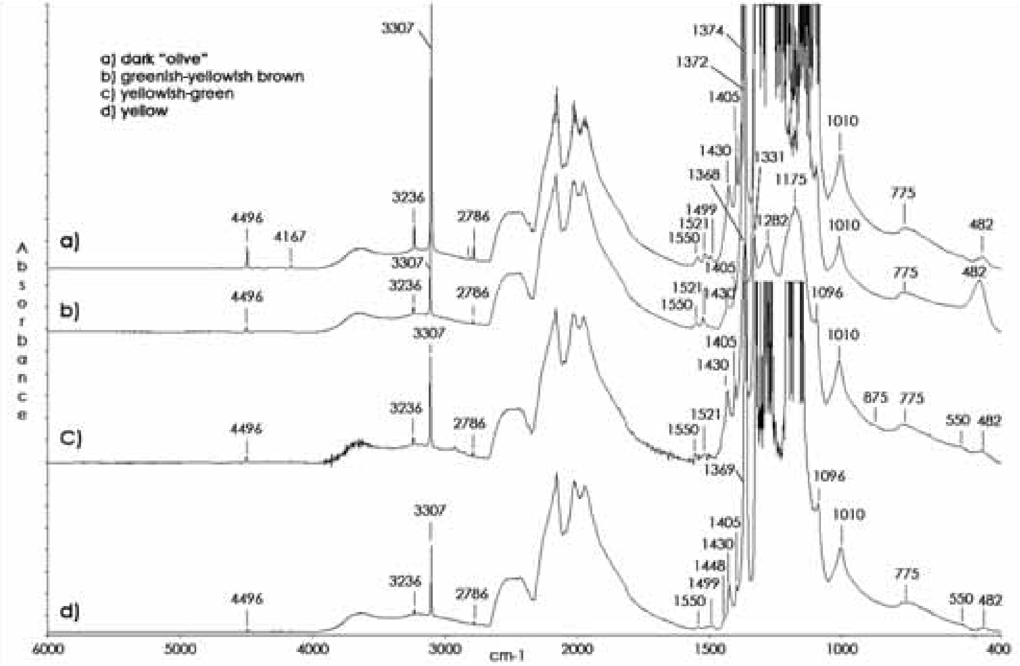

Fig. 2. Main absorptions of the 3107 cm^{-1} system at 1405, 2786, 3107, 4167 and 4496 cm^{-1}, as seen in the infrared spectra of four samples belonging the yellow to brown to green group of H-rich diamonds. The spectra are similar, although the intensities of the individual H-related absorptions and the N-content of the samples vary. The corresponding visible-NIR spectra of the four stones can be seen in Fig. 8.

3. Gray to blue to violet diamonds

Often seen in stones from Argyle, Australia, these spectra are generally characterized by extremely high hydrogen and nitrogen absorptions and very advanced N-aggregation.(39) They are often almost pure type IaB. There is a typically intense 3236 cm^{-1} absorption, occasionally close to the intensity of the 3107 cm^{-1} peak (Fig. 3). Faceted gems in this family are rarely above one carat in mass.

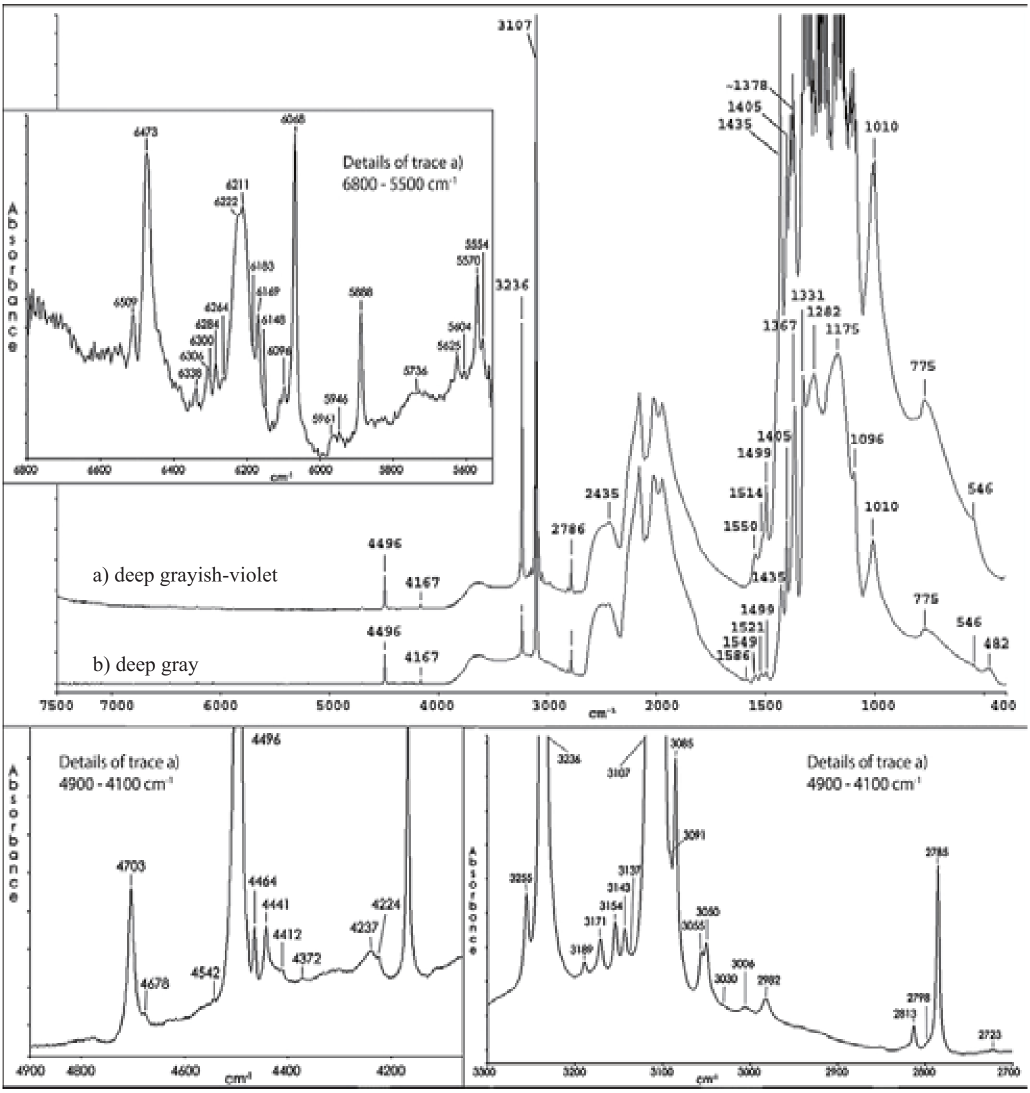

Fig. 3. Infrared spectra of deep grayish-violet (trace a)) and deep gray (trace b)) diamonds from the Argyle mine in Australia with the details of trace a). Although a direct correlation between color and hydrogen / nitrogen content cannot be established, there is a clear tendency for the deeply colored diamonds of this family to be extremely rich in these two impurities. The corresponding visible-NIR spectra of the two diamonds can be seen in Fig. 9.

4. Chameleon diamonds

   Chameleon diamonds have IR spectra that are usually characterized by low to medium nitrogen and hydrogen absorptions (thus are not always H-rich) and a rather low aggregation state; thus, they are frequently type IaA with a Ib character.(40) The hydrogen absorption can be observed as lines of the 3107 cm^{-1} system plus lines attributed to the Ib character.(20)
5. Intense yellow to orange type Ia diamonds

   Diamonds in this group often show an intense coloration and have a characteristic infrared spectrum that shows strong absorptions of the 3107cm^{-1} system plus significant absorptions attributed to a Ib character, and also a rather broad band at 3472 cm^{-1}. Such samples are always nearly pure type IaA of high to very high nitrogen content (Fig. 4).
6. Yellow to orange to brown type Ib and "ABC" diamonds

   The last group is the only one to contain predominantly type Ib diamonds. These diamonds exhibit infrared spectra with a large number of peaks in the spectral regions that correspond to the bending and stretching fundamentals and overtone/combination absorptions of hydrogen.(26) The stones are either type Ib or Ib/aA or Ib/aAB and rich in nitrogen and hydrogen. Such stones are very rare, small, and commonly of very dark color (Fig. 5).

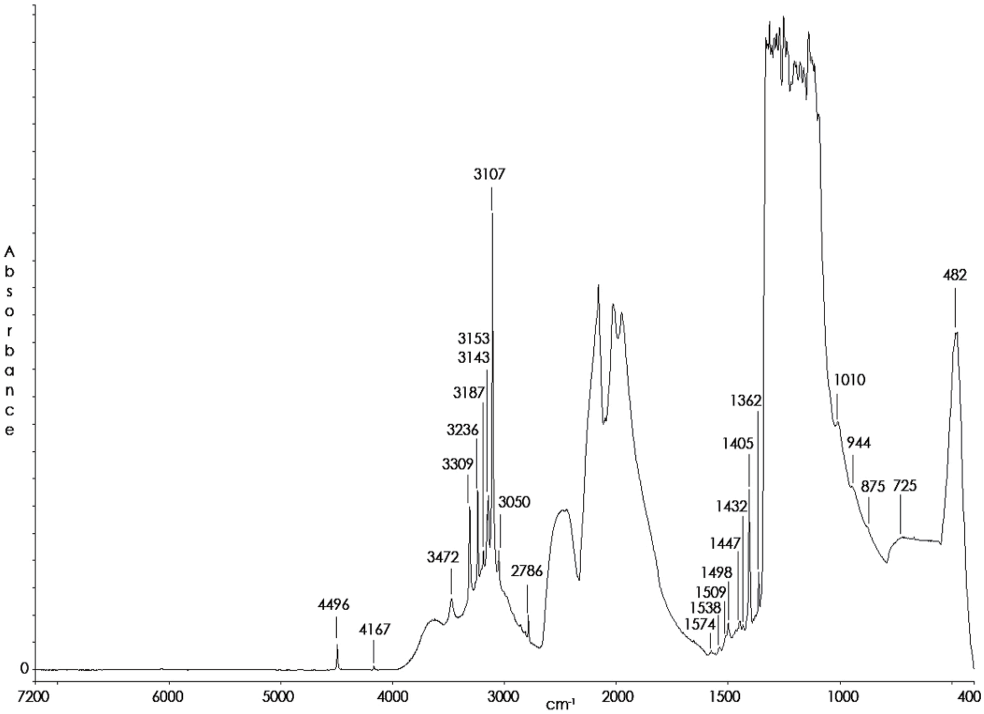

Fig. 4. Infrared spectrum of a H-rich and N-rich intense yellow diamond exhibiting a type Ib character with sharp absorptions at 3309, 3187, 3143 and 3153 cm^{-1}. The corresponding visible-NIR spectra of the sample can be seen in Fig. 12.

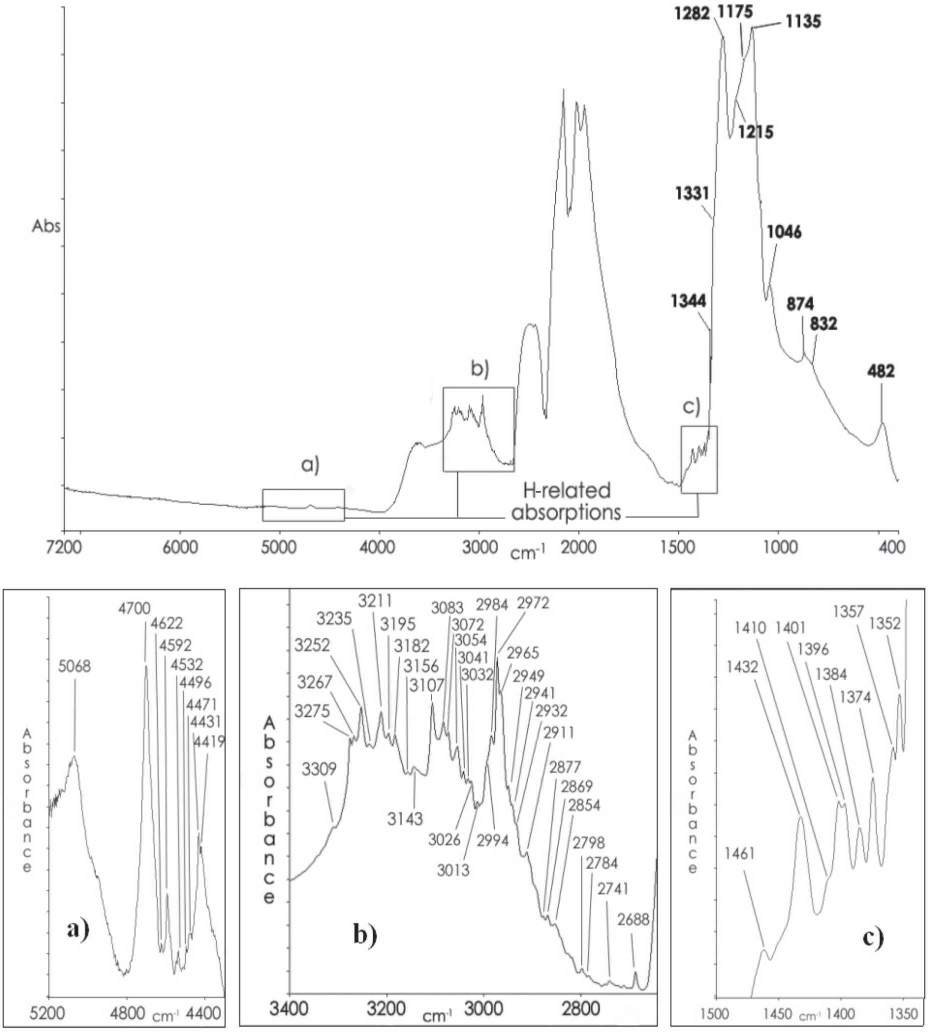

Fig. 5. Infrared spectrum of a predominantly type Ib "ABC diamond" showing details of the many H-related absorptions (a, b and c). The inset b) clearly shows that the predominant H-related absorption is not the 3107 cm^{-1} peak, but the absorption at 2972 cm^{-1}. The corresponding visible-NIR absorption spectrum of the diamond can be seen in Fig. 11, trace a).

3.2 *The system at 3107 cm^{-1}*

The 3107 cm^{-1} absorption peak is very common in natural type Ia diamonds, and always predominates other H-related infrared features. This peak is accompanied by other, less intense peaks (Fig. 3) that are always in the same proportions,(21) thus defining a system. These very sharp absorptions are now classically attributed to the stretching mode (3107cm^{-1}; ν_S) and bending mode (1405 cm^{-1}: ν_B) fundamentals of the C-H group as well as their harmonics and combinations: 2786 cm^{-1}: 2ν_{B}; 4167 cm^{-1}: 3ν_{B}; 4496 cm^{-1}: ν_{S} + ν_{B}; 5555 cm^{-1}: 4 ν_{B}; 5880 cm^{-1}: ν_{S} + 2ν_{B}; and 6070 cm^{-1}: 2ν_{S}.(12,21,23) Although the peak at 5555 cm^{-1} is the weakest of this series, and is therefore rarely detectable,(28) it is found with the strongest 3107 cm^{-1} absorption that is observed for diamonds in group 3. In Figs. 3 and 6, we show spectra demonstrating its presence in stones different from the one in which it was originally described.

A weak absorption at 3098 cm^{-1} is always adjacent to the 3107 cm^{-1} peak, representing about 1% of its intensity.(20) This minor feature has the correct position and intensity to be attributed to ^{13}C-H vibration. The abundance of ^{13}C in natural diamond is about 1.1 %. This validates the attribution to C-H vibration. Furthermore, infrared spectra of a diamond synthesized at high pressure and high temperature (HPHT) with a source of carbon very rich in ^{13}C show peaks at 2757 cm^{-1} (2ν_{B}), 3098 cm^{-1} (ν_{S}) and 4469 cm^{-1} (ν_{S} + ν_{B}) that could be attributed without ambiguity to the ^{13}C-H bond.(28) When ^{14}N is replaced by ^{15}N, no shift of the 3107 cm^{-1} peak is observed.(27) All this suggests that this vibration is a nitrogen-free defect, indicating a C-H bond. However this isotopic argument does not preclude a relationship with nitrogen.(28,41) For comparison, the 1344 cm^{-1} peak, indicating the presence of isolated nitrogen in diamond, does not shift with a change in the isotopic composition of nitrogen.

As mentioned above, theoretical calculations have shown that the defect most likely to induce a vibration at 3107 cm^{-1} is a hydrogen atom located near a bond

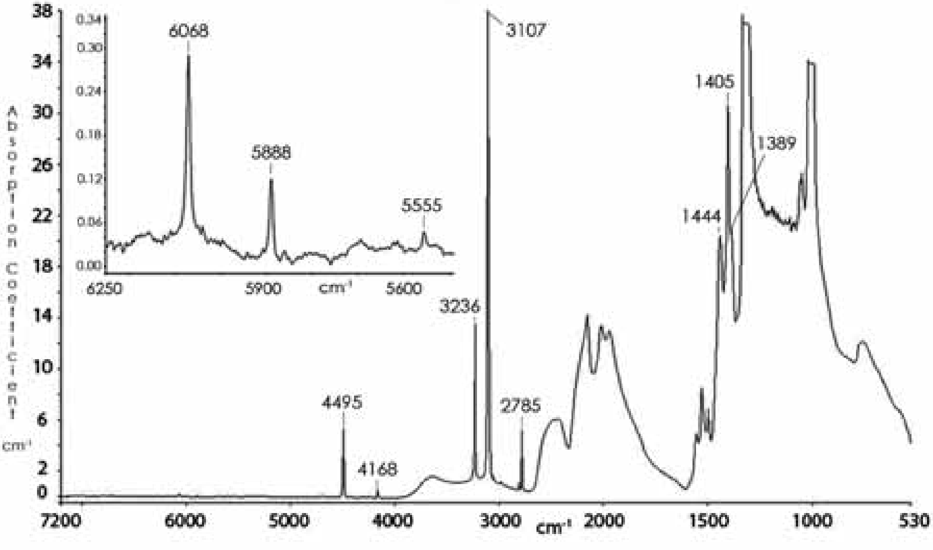

Fig. 6. In this exceptionally H-rich, 0.10 ct grey diamond from Venezuela, the weaker harmonics and combinations of the 3107 cm^{-1} system are visible, including the elusive 5555 cm^{-1} band.

center between N and C.(29,30) The nitrogen involved in the defect is most likely to be aggregated; the 3107 cm^{-1} band appears only when aggregates are present. It does not appear in the spectra of pure type Ib or IIa samples. In our experience, when it is seen in diamonds containing some isolated nitrogen, there are always also some A aggregates present. It has been suggested that in some cases the nitrogen is in the form of an A aggregate, because the 3107 cm^{-1} band correlates in intensity with the concentration of A centers.(24,25,28,42) Nevertheless, the same reasonably intense peak is found in pure type IaB diamonds. The infrared signature of hydrogen in type Ib diamonds significantly differs from that in pure type IaA diamonds.(20) All this strongly indicates a relationship between nitrogen and hydrogen, at least in their infrared active modes, that is likely to be different between type Ia and type Ib samples. Yet, in a HPHT-treated synthetic diamond, a correlation appears to exist between the 3107 cm^{-1} band and total nitrogen content, not just the aggregated N.(27)

3.3 *The system at 3236–4703 cm^{-1}*

The peak at 3236 cm^{-1} is also very frequently observed in type Ia diamonds with a marked absorption at 3107 cm^{-1}. The absorption at 3236 cm^{-1} is best observed in H-rich diamonds from the gray to blue to violet family (Fig. 3).(23) It is never observed in low-nitrogen diamonds. This absorption intensity seems to be higher for type IaB diamonds, whatever their color. Figure 7 shows that the intensity of the peak at 3236 cm^{-1} is proportional to that of the peak at 4703 cm^{-1} from diamonds of the gray to blue to violet family. Hence, we propose that the two peaks stem from the same defect.

The 3236 cm^{-1} band has been alternatively attributed to the amine group N-H bond(20,28) or to the vibration of hydrogen attached to a C-C triple bond group, or alkyne group.(24) It is well known that the absorptions of these two groups appear at approximately the same place, but the N-H vibration is usually much broader.(43) However, because this species would be very dilute in diamond, its absorption might be sharp(44) due to the lack of hydrogen bonding with neighboring groups, as found in polymers, for example.(45) Furthermore, if a stretching vibration is observed, a corresponding bending should be present in the range of 1650–1580 cm^{-1} for the amine and 730–575 cm^{-1} for the alkyne.(43) Although this vibration is expected to be weaker, no such bands have been reported so far in these regions. If one takes into account the 3236–4703 cm^{-1} correlation discussed above, it is very similar to that of the 3107 cm^{-1} fundamental with its first combination band. By assuming that the 4703 cm^{-1} peak also represents the first combination band, with the 3236 cm^{-1} peak being one of the two fundamentals, the other fundamental should be at an energy slightly above 1467 cm^{-1}, consistent with that of an amine group. The presence of an alkyne is therefore less likely, also because such a defect would have to be bound by a single C-C bond to the diamond structure. If this system is indeed due to N-H vibration, then one has to explain why it is not seen in low-nitrogen diamonds.

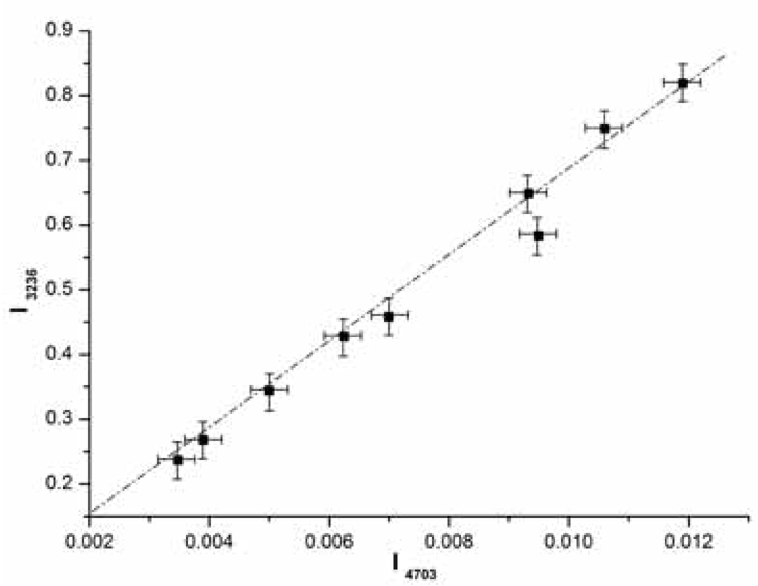

Fig. 7. Graph $I_{3236} = f(I_{4703})$ showing the linear relationship between the 3236 and 4703 cm^{-1} peak intensities.

3.4 *Infrared absorptions related to type Ib character*

In a diamond showing a pronounced type Ib character, Woods and Collins attributed sharp peaks at 3394, 3372, 3343, 3310, 3181, 3145 and 3137 cm^{-1} (Fig. 4) to the stretching mode of the N-H bond.(20) These authors caution that the peaks below 3300 cm^{-1} could also be due to C-H, and the 3309 cm^{-1} absorption could be attributed to the stretching mode of the C-H bond of the acetylene group. However, up to now, no systematic study has been carried out to show the specific characteristics of H-related absorptions in type Ib natural diamonds. Also, considering the recent calculations of Goss *et al.*, the 3145 and 3137 cm^{-1} bands would be good candidates for the stretching vibrations of C-H weakly bonded to an isolated nitrogen (the 3107 cm^{-1} line being apparently associated with aggregated nitrogen only).(29)

Another question of interest is whether the presence of part or all of these bands, in particular, those at 3145 and 3181 cm^{-1}, seen in a number of gems as weak peaks, could indicate with certainty a weak type Ib character. This is of interest to gemologists for determining a partial type Ib character in the absence of other easily discernable absorptions, in particular, in the one-phonon region, when nitrogen-related absorptions are high or atypical (such as in Fig. 4) and the characteristic telltale absorptions at 1344 and 1130 cm^{-1} cannot be seen. In our experience, the presence of these bands is at least consistent with a partial type Ib character, when this can be indirectly determined by gemological properties such as color, color distribution, shape of the UV-visible absorption spectrum or luminescence similar to those observed in diamond for which the type Ib character can be established without doubt.

In some rare, apparently heavily treated (irradiated and annealed) gems, 3145 and 3310 cm^{-1} are the only intense bands, and their heights appear to be correlated, at least qualitatively. It is unclear whether this is the result of the treatment because, so far, this has not been observed in stones that are not treated. This suggests that the group of seven bands correlating to a type Ib character is perhaps not a system, but that several of its bands can act as a system.

Hainschwang *et al*. have studied nine very rare, high-nitrogen type Ib and type Ib/IaAB diamonds ("ABC diamonds") of which all except one sample exhibited a large number of previously undescribed sharp absorptions (of highly variable intensity) in the stretching, bending and combination/overtone regions associated with H-related features.(26) A total of 51 sharp absorptions were reported, of which 47 were tentatively concluded to be H-related and of which 41 had not been previously described (Fig. 5, Table 1). The presence of these peaks in a sample lacking aggregated nitrogen but showing type Ib character with a low single N content of 20 ppm indicates that all these absorptions are most likely to be related to single nitrogen. Nevertheless, their intensity appeared not to be directly correlated with the quantity of single nitrogen detected. The most intense line found in such diamonds is an absorption peak at 2972 cm^{-1}. Such diamonds may be considered as H-rich type Ib.

3.5 *Minor systems*

Some weaker lines have sometimes been observed together in some samples. Few of them have been subjected to a systematic analysis to establish whether they are correlated. Nonetheless we present them as systems, as long as they have not been proven to be noncorrelated.

* 3050 and 3155 cm^{-1}

These peaks were detected together in the cuboid growth sectors of mixed-habit diamonds, but not in adjacent octahedral growth sectors.(25) Their relative intensities proved that they are, in general, independent from the 3107 cm^{-1} and 3236 cm^{-1} systems. However, in some samples, they vary positively with the 3236 cm^{-1} system. It has been proposed that they reflect the same H-related defect.

* 3055 and 2982 cm^{-1} observed in "reverse chameleon" diamonds with high concentrations of nitrogen, described by Hainschwang *et al*., and seen in H-rich gray to violet diamonds from Argyle by one of the authors (TH).(40) The 3055 cm^{-1} peak often forms a doublet with the 3050 cm^{-1} band (see Fig. 3). Reverse chameleon diamonds, which only exhibit a thermochromic color change from yellow to green-yellow, were shown to be spectrally closely related to the gray to violet H-rich diamonds from Argyle.(46)

3.6 *Isolated lines*

Many additional, much weaker peaks have been observed in H-rich diamonds. Nonetheless, their weak intensities make them difficult to study, and it is even more difficult to correlate them. We give several examples below.

A weak absorption at 2850 cm^{-1} was detected in the infrared spectra of some diamonds from Argyle(24) and in some asteriated diamonds.(25)

A recent systematic study of hydrogen in natural diamonds(38) revealed the presence of numerous additional absorption lines previously undescribed. Because they are most clearly observed in H-rich diamonds, they are tentatively related to some H-related defects. They seem to form two groups. The first is in the range 2700–3600 cm^{-1} with absorptions at 2722, 2750, 2859, 2944, 3006, 3030, 3069, 3086, 3162, 3197, 3208, 3214, 3262 and 3286 cm^{-1} (some can be seen in Fig. 3). The second spans from 4000 to 7000 cm^{-1}, with absorptions at 4224, 4240, 4412, 4440, 4453, 4464, 4522, 4532, 4546, 4572, 4588, 4630, 4668, 4702 and 4722 cm^{-1} with, in addition, absorptions at 5570, 5626, 6214 and 6474 cm^{-1}. Many absorptions of this second group are visible in Fig. 3.

A complete list of bands at least tentatively attributed to H-related defects is provided in Table 1. Because of differences in instrument or in the choice of the apparent maximum, bands indicated in the literature at different, but close positions may be the same. When we consider, on the basis of our experience, that the different positions given in the literature correspond to the same band, they are listed in the same cell.

4. Hydrogen-Related Defects Active in the UV-Visible-Near-IR Part of the Spectrum

H-related defects causing absorption in the UV-visible-near-infrared (UV-Visible-NIR) range are found exclusively in H-rich type I diamonds. This physical character could possibly be used as part of the definition of this group. Three main families of absorption spectra were originally defined,(23,31) the first of which has recently been slightly extended.(38)

1. The brown to grayish-yellow to green family
2. The gray to blue to violet family
3. Chameleon diamonds

4.1 *Brown to grayish-yellow to green family*

Diamonds belonging to this family present a typical UV visible spectrum (Fig. 8). This spectrum is characterized by an absorption continuum increasing from the red toward the violet, which accounts for much of the absorption. This induces a brown or yellow color, depending on whether the slope is weak or moderate. The largest brown diamond of this family (free of the brown graining typical of most natural brown diamonds) is the Eye of the Tiger, a 61 ct round brilliant.(47) Yellow diamonds belonging to this family constitute about 4% of all yellow diamonds.(48,49) There is also a very broad complex absorption centered between 700 and 750 nm, with a broad “triple band” tail with maxima at 825, 836 and 845 nm.(40) This is responsible for the green component of the color and the recent extension of this family,(38) which was originally named “brown to grayish yellow.” Note that green H-rich diamonds had already been mentioned by Fritsch,(50) but they were assigned to the gray to blue to violet family. When both of these broad light-absorbing features are of comparable importance, the color is brownish green and is sometimes referred to as “olive” in the diamond trade. Numerous weaker,

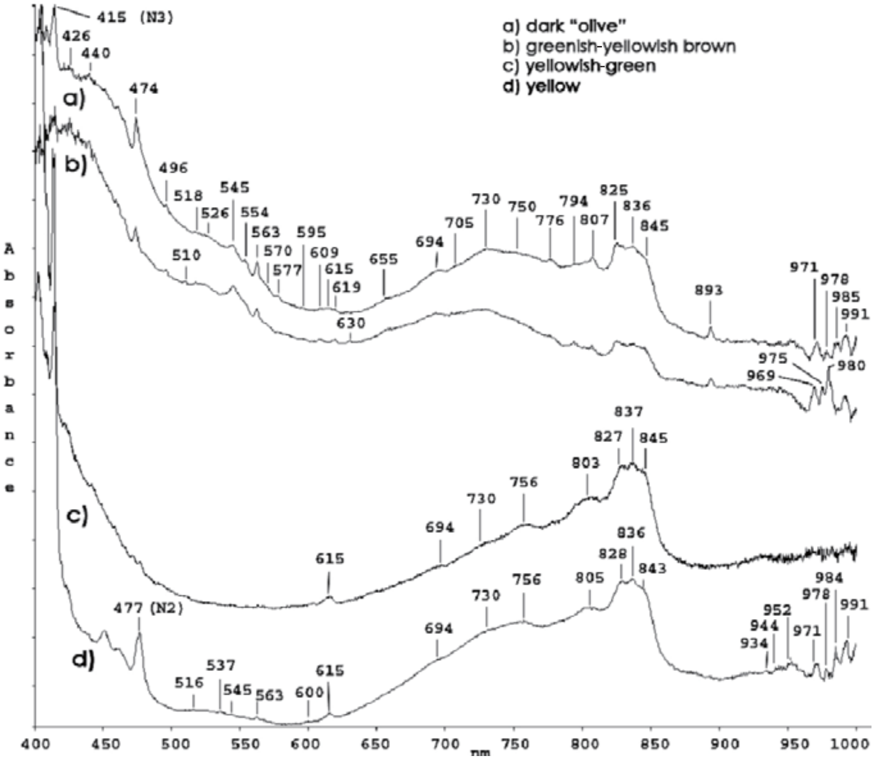

Fig. 8. Visible-NIR spectra representing the colors of the "brown to grayish-yellow to green family." The spectra demonstrate that the colors depend mainly on the intensity of the continuum, the 730–750 nm band and the N3 and N2 centers. The corresponding FTIR spectra (recorded for the same stones) can be seen in Fig. 2.

sharper absorptions at, for example, 563, 555, 545, 474, 440 and 432 nm are present, but do not contribute significantly to the color. Further bands toward the UV were found by Rondeau *et al.* in one thin cleavage, at about 387, 371, 367, 363, 360 and 357 nm, and may be also H-related.(25) All these features have been proposed to be H-related.(23) The 554 nm absorption combined with the 545 nm peak and bands at 525 and 518 nm cause, when they are sufficiently intense, a weak broad band centered at ±550 nm.

Such diamonds also often show intense sharp absorptions at 969, 975, 980 and 991 nm and weak peaks at 426, 496, 510, 609, 618, 630, 655, 694, 776, 794, 807, 893, 916, 934, 944 and 952 nm.(40,51)

Some additional, nonspecific UV-visible absorptions are usually observed: moderate to strong N3 center absorption (ZPL at 415.2 nm and its vibronic phonon sidebands at 403.6, 394.6, 384.5 and 375.8 nm), the N2 center (ZPL at 477.6 nm with vibronic phonon sidebands at 462 and 452 nm), the N5 center (329.6 nm), the N4 center (344.2 nm) and the S3 center (496.7 nm). A strong N3 / N2 center enhances the yellow color of the sample.

4.2 *Gray to blue to violet family*

Typical visible-NIR spectra of diamonds belonging to this family are shown in Fig. 9. These spectra are characterized by the presence of numerous complex broad-band systems. The two most important ones are centered between 730 and 750 nm and between 520 and 565 nm. Relatively intense broad bands occur at 836 nm (a triple band composed of 829, 837 and 844 nm absorptions, similar to that seen in the previous family) and 945 nm, and there are intense sharp absorptions at 969, 975, 979 and 991 nm. Further characteristic spectral features include weak absorptions at 425, 443, 594, 608, 617 and 631 nm, and weak broad bands at 786, 806, 883 and 916 nm. Some of these features were described by Iakoubovskii and Adriaenssens.[(24)]

The most important features that distinguish this family from the previous one are the presence of the rather intense "520 to 565 nm" band, the usually much higher intensity of

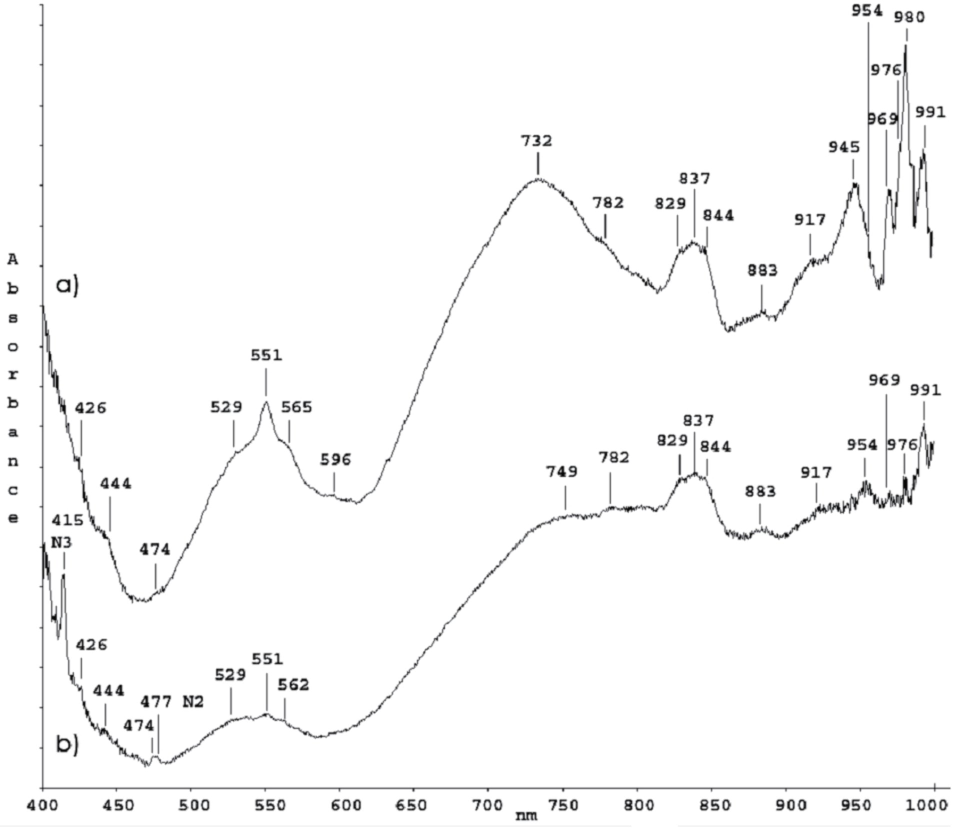

Fig. 9. Visible-NIR spectra of a deep grayish-violet (trace a)) and a deep gray diamond (trace b)). The 520–565 nm band and the 730–750 nm band define the two transmission windows, in the blue and the red regions, respectively, and are responsible for the observed color if they are sufficiently strong. Otherwise, the average high absorption throughout the visible region produces a gray color. The corresponding infrared spectra of the two stones can be seen in Fig. 3.

the “730 to 750 nm” band, and the generally very weak or absent N3 and N2 absorptions. Additionally, many of the sharp weak absorptions seen in the spectra of the “brown to grayish-yellow to green” family are not found. Globally seen, the spectra of the two families are often similar in the 600 to 1000 nm range (except for band intensities) but differ in the 400 to 600 nm range.

The color of diamonds belonging to this family of H-rich diamonds is explained by the ratio of the two broad transmittance bands centered in the blue region at about 470 nm and in the red-orange region at about 610 nm. These transmission windows are often not very marked; thus, the absorption is roughly constant throughout the visible region, giving rise to the predominant gray color (the scale in Fig. 9, designed to emphasize weak features, may be misleading in that regard). The blue color is due to the blue transmission being clearly predominant. The “blue” color of these diamonds has been directly associated with the high hydrogen content by Iakoubovskii and Adriaenssens.(24) The violet appearance, sought after by collectors, results from a more balanced transmission in the two windows, the blue being more marked than the red. By contrast to the graining-colored purple diamonds that transmit light from about 600 nm to the mid infrared region,(50) violet diamonds absorb strongly from around 650 to 800 nm. Thus, these diamonds appear violet not because of transmission in the violet part of the spectrum, but because of the balance of blue and red transmission bands. Therefore, the observed color is not a spectral one. The N3 center is sometimes observed.

4.3 *Chameleon diamonds*

Chameleon diamonds change color when they are heated above 140°C (thermochroism phenomenon), or when they are kept in the dark for some time from a few hours to a few days (photochroism phenomenon).(40) The color typically changes from a grayish-green to a yellow or orangy-yellow color, often with a brownish modifying hue.(38,40,52) Chameleon diamonds could possibly be classified as part of the “brown to grayish-yellow to green” family, but their very special behavior justifies describing them as a separate family.(52)

Their very specific UV visible spectrum shows a continuum of absorption increasing from the green to the UV region, a very broad band that extends from the orange to the near-infrared regions, centered at around 800 nm, a weak, broad band centered at about 480 nm and a weak and sharp (possibly companion) line at about 426 nm (Fig. 10). All diamonds (including chameleon diamonds but not exclusively) showing the 480 nm (2.6 eV) absorption band exhibit an intense chalky white to yellow to orangy-yellow fluorescence as well as intense and long-lasting phosphorescence of a similar color.(53) Additional, weak and mostly sharp absorptions at 523, 546, 563, 570, 583, 648, 664, 767, 775 and 792 nm are sometimes observed, of which some belong to the brown to grayish-yellow to green family.(23) The 648, 767 and 792 nm features are related to Ni.(54)

As a matter of fact, all chameleon diamonds contain hydrogen but are not always H-rich.(40) It would be interesting to check whether chameleons that are not H-rich result from mixed growth (this is very often the case in our experience). In that case, the cuboid sectors may be H-rich, but the stone’s spectrum, averaged over all sectors, may not fit the defining criterion.

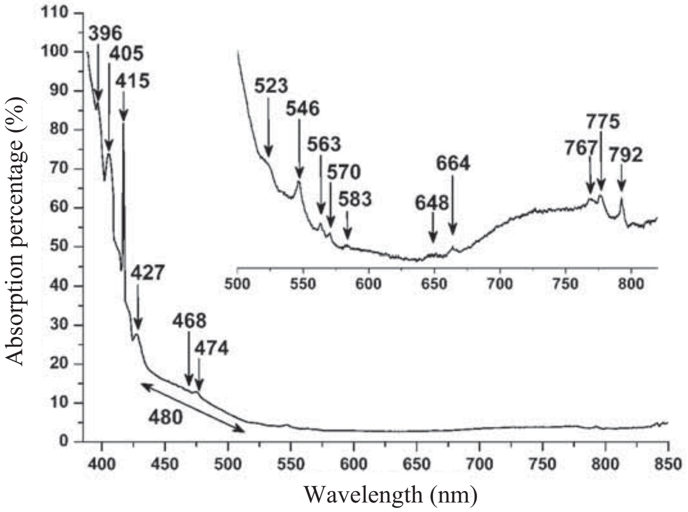

Fig. 10. UV-visible spectrum of the 22-ct chameleon diamond at liquid-nitrogen temperature (green state).

The two additional families described below do not exhibit color-producing H-related defects, but their visible or near-infrared spectra may show some H-related absorptions.

Group 6 of the yellow to orange to brown type Ib and "ABC" diamonds includes some very rare predominantly type Ib diamonds with absorptions in the NIR range from 733 to 905 nm that have been correlated with infrared-active hydrogen.(26) The predominant defect that these authors described as being associated with H-rich type Ib diamond is the "905 nm center" with phonon sidebands at 880, 867, 847 and 806 nm (Fig. 11).

Finally, group 5 of the intense yellow to orange type Ia diamonds includes diamonds very rich in infrared-active hydrogen that typically only show a continuum of absorption regularly increasing towards the UV range with a strong slope, as in type Ib stones. Usually, there is no distinct band that could be attributed to a defect involving hydrogen.(38) In some cases, such diamonds exhibit multiple sharp and usually very weak absorptions, which are similar to those observed for the brown to grayish-yellow to green family (Fig. 12). Such diamonds include a series of H-rich cuboid diamonds known to come from the Democratic Republic of Congo (formerly Zaire).

The noncorrelation of infrared-active hydrogen with the presence and intensity of absorptions in the UV-visible-NIR range has been demonstrated (*e.g.*, ref. 38). The observation of diamonds very rich in hydrogen but lacking distinct H-related absorptions in the UV-visible-NIR spectrum clearly indicates that the defects responsible for color in these samples differ from the defects causing absorption in the infrared spectra.

The correlation of hydrogen with nitrogen content and the frequent detection of nickel, by photoluminescence (PL) and energy dispersion X-ray fluorescence (EDXRF) spectroscopy, in H-rich diamonds may indicate that the defects responsible for the UV-

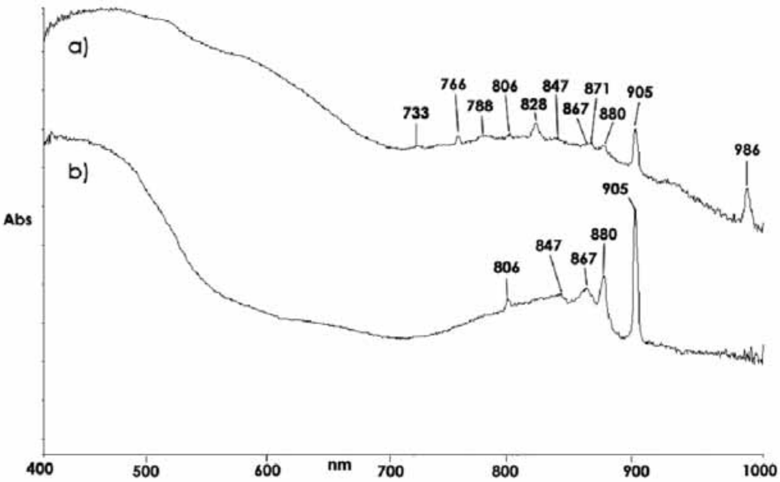

Fig. 11. Visible-NIR spectra of two H-rich, predominantly type Ib diamonds. The stone in trace a) contains high concentrations of single nitrogen plus A aggregates and some B aggregates (see Fig. 5 for its FTIR spectrum), and thus exhibits the H2 center, while the stone in trace b) is low in single nitrogen and shows no trace of aggregated nitrogen.

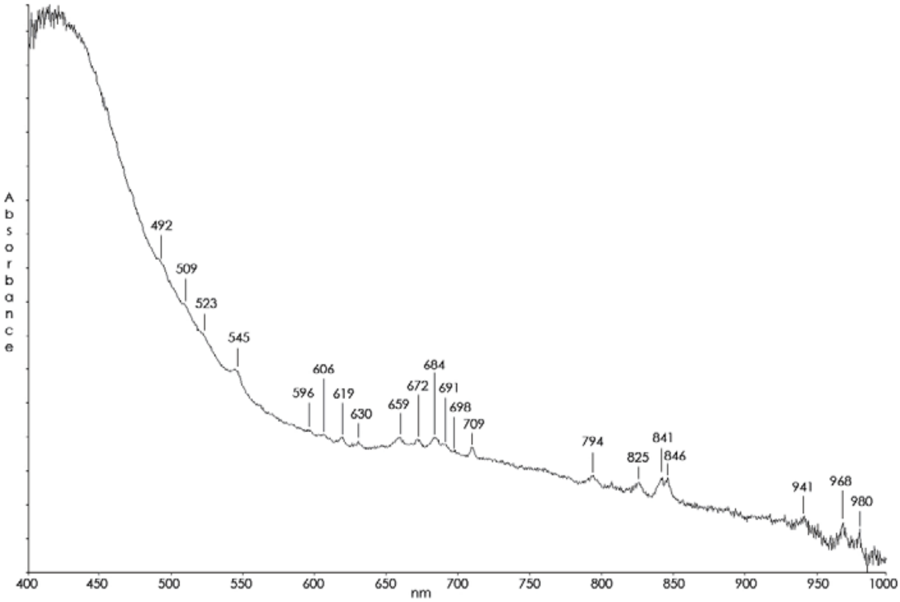

Fig. 12. Visible-NIR spectrum of an intense yellow H-rich diamond of type IaA with Ib character. The spectrum indicates that the stone is essentially colored by the “type Ib” baseline. The many absorptions of weak intensity nominally contribute to the color of the diamond. Often such diamonds do not show any absorption peaks apart from the continuous “type Ib” band. The stone’s infrared spectrum can be seen in Fig. 4.

visible-NIR absorptions involve not only hydrogen, but also nitrogen and possibly nickel. Nickel has been detected in chameleon diamonds,(40) in H-containing type Ib diamonds,(55) in H-rich type Ia yellow diamonds(56) and in gray to blue to violet diamonds.(24,39) Although a clear correlation between color intensity and infrared active hydrogen content could not be determined in such diamonds, it is apparent that the darkest colors caused by complex absorptions in the UV-visible-NIR range are observed in diamonds having the highest N and H contents, but not necessarily the highest nickel content. This observation confirms that hydrogen plays an essential role in the coloration of such diamonds, but nickel is a possible candidate for some of the defects involved.

The “brown to grayish-yellow to green” and the “gray to blue to violet” families differ in that the N3 and N2 centers are often (but not always) distinct in the first family, while they are generally very weak or absent in the second one. This is surprising since both have very similar infrared spectra with high H and N contents and nitrogen in an advanced state of aggregation. However, in general, the aggregation state is even more advanced in the gray to blue to violet samples. The N3 center has been defined as a side product of the aggregation of A aggregates into B aggregates.(57) This would imply the presence of a distinct N3 center in pure type IaB diamonds of the second family. Yet, these samples only rarely exhibit an N3 center. The proposal by Kiflawi and Bruley(58) that an N3 center is more an intermediate product than a side product of A center to B center transformation would explain why pure type IaB diamonds of the gray to blue to violet family are free of N3 defects, since, on the basis of this theory, complete nitrogen aggregation would also transform the N3 centers into B aggregates.

The main difference between the two groups is the presence of intense 520 to 560 nm absorptions in the gray to blue to violet family, while a band in this spectral range is practically absent in the other family. One possible interpretation (out of many) of the complex feature with maxima in the 520 to 565 nm range is to consider it a reaction product of the N3 center with hydrogen. This would explain why such a feature is statistically present when the N3 center is absent, or, more correctly, no longer present.

5. Luminescence Centers

H-rich natural diamonds usually show a yellow to green luminescence (e.g., ref. 22). This is due, at least in part, to the presence of nickel-related S1 and S3 defects. The S3 defect consists of a Ni^+ ion in a divacancy surrounded by two or three nitrogen atoms in the nearest coordination sphere.(59,60) More generally, nickel has been proven to be associated with nitrogen in several optical defects in both natural and synthetic diamond,(24,36,60–66) which are better studied by electron paramagnetic resonance (EPR). Theoretical calculations offer precise information regarding the nature of these defects.(67) Because nickel is strongly associated with cuboid growth sectors in natural diamond,(1) and hence to H-rich diamond, it can be suggested that there is a relationship between hydrogen and nickel. For example, it has been proposed that hydrogen could play a role as a distant charge compensator in the broadening of EPR lines observed in H-rich natural diamonds.(36) Yet, the influence of hydrogen on nickel-related luminescence centers remains unclear.

The long-lasting phosphorescence associated with H-rich chameleon diamonds is an identifying characteristic of such gems. Yet, yellow phosphorescence in and of itself is not related to hydrogen, because it is the emission associated with the 480 nm broad band. However, the emission lifetime is at least visually much longer in chameleon diamonds, suggesting that hydrogen may have provided some deeper traps responsible for the longer phosphorescence.

We know of no luminescence center directly related to the hydrogen impurity. However, observations suggest that hydrogen may play an indirect role in photoluminescence processes.

6. Discussion

It is a striking realization that, although the 3107 cm^{-1} system was identified 47 years ago, we are still not completely certain of the structure of the defect responsible for these absorptions. If this is true for the main H-related absorptions, it is, a fortiori, also valid for all other H-related absorptions, from UV to IR, which have been less studied. Several avenues of research can be followed to further our knowledge. First of all, it is apparent that work at higher resolution in the infrared region, possibly down to 0.5 cm^{-1}, but still with acceptable signal-to-noise ratios, will produce more details (weaker bands) which may help in constraining interpretation, and allow a more quantitative approach in terms of bandwidth and absolute absorbance, for example. Also, a more systematic study of some of the systems described here will add to the understanding of which bands are truly related. In particular, it would be beneficial to try to correlate infrared bands with other physical properties, such as UV-visible absorption (color), luminescence, growth sectors (as seen in cathodoluminescence, for example) and the incorporation of other defects such as N and Ni. On a more theoretical side, it would be valuable to pursue calculations of defect stability, and to compare H-related defects in natural diamond with known H-related defects in silicon or other diamond analogs, in order to predict or validate potential models for those defects that show absorbance from the UV to IR regions and those that do not. This would contribute to determining the nature of optically inactive hydrogen reservoirs in the diamond structure. One could then seek suitable physical methods for proving their existence, and perhaps quantify them.

Although the point has only been made for the 3236 cm^{-1} system here, all bands that are tentatively interpreted as the stretching modes of C-H or N-H bonds should have a corresponding bending mode, and possibly overtones and combinations. Although it is assumed that these other modes should induce weaker absorptions, these should possibly appear on spectra acquired at higher resolution or lower temperature or both.

The criterion used to define H-rich diamond also needs to be refined. For example, in the study by Rondeau *et al.*(25) it is apparent that the octahedral sectors of an asteriated diamond should be H-rich from the height of the 3107 cm^{-1} band, according to the 1991 definition, but they show no such character. Perhaps the concept should be refined per growth sector with different thresholds for octahedral and cuboid growth sectors; then, for example, the threshold would be an absorption at 3107 cm^{-1} superior to 3 cm^{-1} at 4 cm^{-1} resolution for the octahedral sectors in ref. 25. The simple fact that H-related absorptions are induced in the visible range may serve as a criterion in some cases. One could also propose a definition based on absolute hydrogen concentration.

This raises the point of concentration calibration of the absorption of the 3107 cm^{-1} system, and other H-related bands as well. Hydrogen is often present in nominally anhydrous minerals in very small amounts, yet it influences the physical and chemical properties of the host material to an extent far disproportionate to its low concentration.(68,69) There is no convenient measure of this parameter at this time, but this problem is general and not limited to diamond even if nuclear or ionic methods are presently the best candidates for solving this problem.(68) It can be suggested, from a review of the literature, that most H-rich type Ia diamonds probably contain on the order of 500 to 1000 atomic ppm hydrogen.(18,24,25)

Also, there is no real understanding of the causal relationship between cuboid growth and preferred hydrogen incorporation. This relationship would be understood if a synthetic cuboid diamond could be produced, a new challenge for specialists of HPHT synthesis, such as the editor of this special issue. It would then provide insight into the geological environment needed to obtain such a diamond. Conversely, if cuboid diamonds could be found in their mother rocks, such as in xenoliths, studying the associated mineralogy and its hydrogen or “water” content would provide some answers. There is a need for the extensive systematization of cuboid growth with regard to hydrogen content, from “normal” diamonds with cuboid growth episodes to H-rich diamonds. Also, more will be learned about the cuboid growth mode by comparing cuboid and octahedral sectors grown simultaneously (in asteriated diamonds) in terms of N, H and Ni concentrations, for example.

7. Conclusions and Summary

Several H-related absorption systems have been defined up to now in natural diamond. In the infrared region, the most important is the 3107 cm^{-1} system, with companion lines at 1405, 2786, 4167, 4496, 5555, 5880 and 6070 cm^{-1}. The system most likely corresponds to a C-H vibration bonded to some form of aggregated nitrogen. Other infrared systems seen in type Ia diamonds include the 3236–4703 cm^{-1} (probably corresponding to a N-H vibration), 3050–3155 cm^{-1} and 3055–2982 cm^{-1} systems. A number of other typically rare, weak and sharp bands are believed to be due to H-related defects.

Sharp lines at 3394, 3372, 3343, 3310, 3181, 3145 and 3137 cm^{-1} are apparently exclusively seen in type Ib diamonds (or diamonds with a partial Ib character) and are likely to correspond to some sort of N-H stretching. More than 40 new H-related absorptions distinct from the ones present in the infrared spectra of type Ia diamonds have been found in some dark type Ib diamonds. The H-rich type Ib diamonds are much rarer than H-rich type Ia diamonds, and samples are almost always small (below 0.1 ct in mass) and dark.

On the basis of the spectral and optical properties, roughly 6 groups of H-containing diamonds have been defined, of which only one is common. The three color families with UV-visible-NIR active H-related defects are the “brown to grayish-yellow to green” family, the “gray to blue to violet” family, and the “chameleon” family. Although the nature of the relevant defects at the atomic level is not known, there appears to be a partial correlation between the hydrogen detected in the FTIR spectra and the depth of color; the darkest H-rich diamonds are always extremely rich in hydrogen and nitrogen.

All these H-rich diamonds probably result from cuboid growth, which preferentially incorporates hydrogen compared to octahedral growth.

To help in future work regarding H-related defects in diamond, we propose, for quantitative purposes, that infrared spectra be acquired at a higher resolution than the standard 4 cm^{-1}, down to 0.5 cm^{-1} if possible. Also, it should be useful to refer to the tentative classification we have proposed, which provides relevant details about color, color distribution, growth morphology and UV-excited luminescence, as well as UV-visible-NIR and infrared spectra.

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