

## Conformation of hydrogen in deep earth\*

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Hydrogen is the simplest atom and the most abundant element in the universe. Molecular hydrogen is a common form of hydrogen. The phase transition of molecular hydrogen at the ultrahigh pressure is the subject of great theoretical and experimental interest in the 1980's. However, whether there exists molecular hydrogen in deep earth is an important problem. This paper presents our recent results.

We have found the peaks of molecular hydrogen (?) by Raman spectroscopy in diamonds from Liaoning<sup>[1]</sup> and Hunan Provinces following the discovery of potassium-, sodium- and copper-bearing chloride inclusions in diamonds<sup>[2-4]</sup>. These diamonds have not any fractures. The characteristics of these diamond samples and their Raman spectral peaks are shown in table 1 and figure 1.

Table 1 Characteristics of molecular hydrogen-bearing diamond and its Raman spectral peaks

No.	Type	Absorption limit/nm	Crystal form	Colour	Inclusion	Raman spectral peak/cm <sup>-1</sup>
L182	I <sub>a</sub>	300	RD	CN	two transparent small inclusions	4 190, 3 968
H305	I <sub>a</sub>	297	RD	CN	many little green inclusions	4 200, 3 978
H324	I <sub>a</sub>	298	RD	CN	many large, little green inclusions	4 198, 3 978
H328	II <sub>a</sub>	225	OC	CN	little black inclusions	4 198, 3 954

RD, Rhombic dodecahedral; OC, octahedral, CN, colourness.

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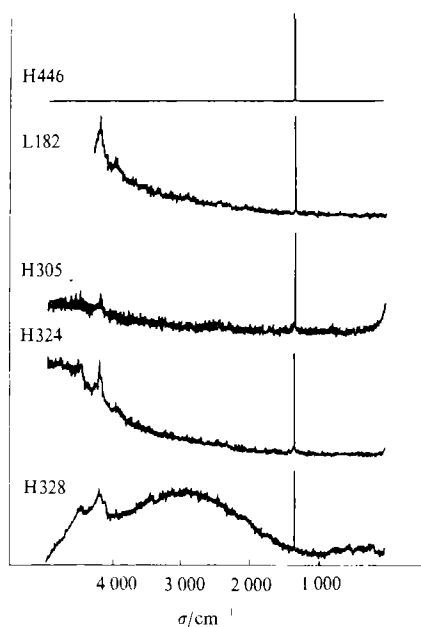


Fig. 1. The Raman spectra of molecular hydrogen-bearing diamonds.

The Raman spectra taken by Model U-1000 laser Raman microprobe spectroscopy show  $4190\text{--}4200\text{ cm}^{-1}$  peaks in many regions of the four diamonds, and  $3940\text{--}3972\text{ cm}^{-1}$  side peaks in some regions. These peaks are all outside the inclusion regions. In fig. 1 sample H446 has no molecular hydrogen.

As for the  $4190\text{--}4200\text{ cm}^{-1}$  peak, there may be two interpretations. The nearest peak is at  $4156.5\text{ cm}^{-1}$  of molecular hydrogen<sup>[5]</sup>. Moreover, Rossman<sup>[6]</sup> indicated that the vibration peak bonded between metallic ion and hydroxyl occurs at  $4200\text{ cm}^{-1}$ . But on the screen of the Raman spectroscopy, the regions where the  $4190\text{ cm}^{-1}$  peak appears show no inclusion and no other peaks of hydroxyl occur on the Raman spectrum. For example, near  $3600\text{ cm}^{-1}$  there appears a broad peak of hydroxyl. Therefore, we rule out the possibility of M-OH bond, and consider that the peak is possibly originated from the stretching vibrational peak  $Q_{1\rightarrow 0}(J)$  with  $v=1$  ( $0\rightarrow 1$ ),  $J=0$  ( $0\rightarrow 0$ ), and  $J=0$ , where  $v$  and  $J$  are the vibrational and rotational quantum numbers, respectively. A similar interpretation of molecular hydrogen by Luth (1987) is used to account for the  $4130\text{ cm}^{-1}$  Raman peak in aluminosilicate glass.

The first problem is that the peak of Raman spectrum of molecular hydrogen in normal temperature and atmospheric pressure is located at  $4156.5\text{ cm}^{-1}$ , but the measured peak appears at  $4190\text{--}4200\text{ cm}^{-1}$ . The wave number error of the instrument is less than  $2\text{--}3\text{ cm}^{-1}$ . It is obvious that the frequency shift of the peak is attributable to high pressure. Hemley and Mao<sup>[7]</sup> reported the frequency shift of the Raman peak of solid molecular

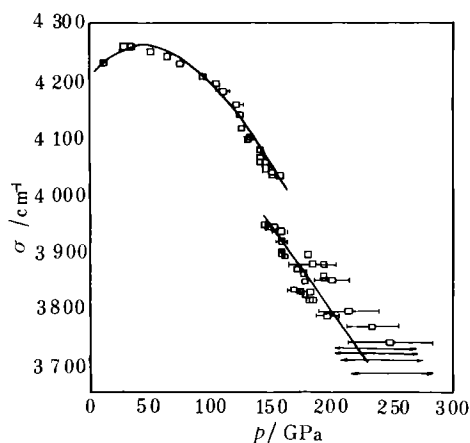


Fig. 2. The dependence of the vibration frequency of the Raman spectra of molecular hydrogen at 77 K on pressure.

hydrogen with changing pressure (fig. 2). At 77 K the wave number of the peak with rising pressure at the beginning increases to  $4\,250\text{ cm}^{-1}$ , and then falls continuously, through insulating hydrogen phase and transitional metallic hydrogen phase, to about  $3\,700\text{ cm}^{-1}$ . Then the  $4\,190\text{--}4\,200\text{ cm}^{-1}$  peak can be interpreted as produced at either relatively low pressure or high pressure.

We first consider the possibility of molecular hydrogen at relatively low pressure. According to Raman peak frequency dependence on pressure at 5 K by Silvera<sup>[8]</sup>, we obtained a result that about 3—4 GPa pressure corresponds to the  $4\,190\text{--}4\,200\text{ cm}^{-1}$  peak of molecular hydrogen at relatively low pressure (fig. 3). But the temperature at which natural diamond grows is commonly higher than 5 K. The temperature of high-pressure synthetic diamond is  $1\,300\text{--}1\,600\text{ }^\circ\text{C}$ , and the growth temperature calculated from inclusions in diamond is more than  $800\text{--}1\,000\text{ }^\circ\text{C}$ . Until now we have not obtained  $>800\text{ }^\circ\text{C}$  high-pressure phase diagram of hydrogen. In consideration of the temperature effect, we consider that 3—4 GPa is only the lower pressure limit of molecular hydrogen in the low pressure region. It appears that low pressure molecular hydrogen in the diamond is in the form of fluid, namely liquid or vapor phase.

For molecular hydrogen in the high-pressure region, the corresponding high-pressure molecular hydrogen is of liquid or solid phase. If the high-pressure molecular hydrogen is of solid phase, then the  $3\,940\text{--}3\,972\text{ cm}^{-1}$  peak can be interpreted at the same time. In fact, materials possessing  $3\,940\text{--}3\,972\text{ cm}^{-1}$  Raman peaks are extremely rare. Lorenzana *et al.*<sup>[9]</sup>, Mao and Hemley<sup>[10]</sup> reported that in the phase transition region of insulating hydrogen to metallic hydrogen at 77 K (fig. 4), there are two Raman peaks, metallic hydrogen peak at  $3\,935\text{--}3\,950\text{ cm}^{-1}$ , and insulating hydrogen peak at  $4\,050\text{--}4\,070\text{ cm}^{-1}$ . The former is near the determined  $3\,940\text{--}3\,972\text{ cm}^{-1}$  peak. Then the two peaks we deter-

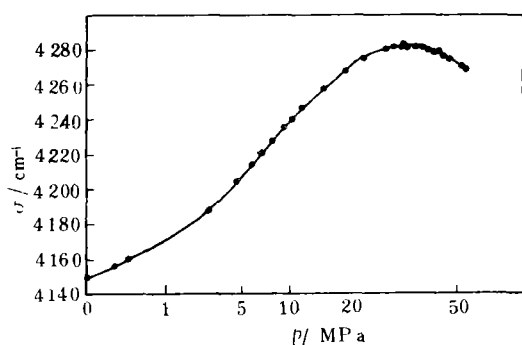


Fig. 3. The Raman peak frequency dependence on pressure of the molecular hydrogen in the lower pressure region at 5 K.

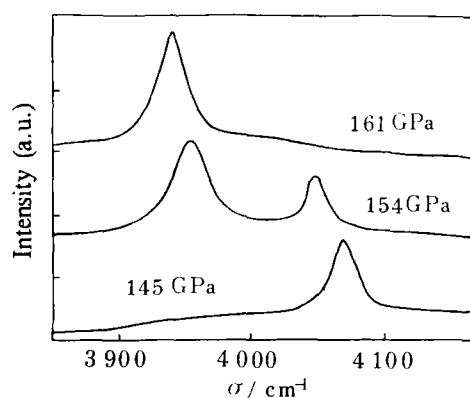


Fig. 4. The Raman peak frequency dependence on pressure of the molecular hydrogen in the solid phase transition region at 77 K.

mined can correspond to the peaks in the phase transition region of molecular hydrogen. Then the pressure of molecular hydrogen in the high-pressure region should reach 150 GPa or higher. Ruoff *et al.*<sup>[11, 12]</sup> reported the stability of type I<sub>a</sub> and type II<sub>a</sub> diamonds at 416 GPa and 338 GPa, respectively. It is shown that the pressure at which the diamond is formed may reach 150 GPa, but it should be further confirmed. If we do not consider the second peak, the 100 GPa pressure is corresponding to the 4 190—4 200 cm<sup>-1</sup> peak. Then in the high pressure region the corresponding pressure of molecular hydrogen is 100—150 GPa or more.

Although the hydrogen-bearing diamond has been reported<sup>[13, 14]</sup>, it is considered that hydrogen takes the form of C—H and N—H compounds. The existence of molecular hydrogen means that the hydrogen takes the form of either compounds or elements. It may be seen that the activity of hydrogen should play an important role in the chemical reaction in deep earth.

In recent years, studies of mantle metasomatism and mantle fluids show that they would affect the composition of the mantle, partial melting, generation of magma and mantle plumes. In general, mantle fluid responsible for mantle metasomatism is composed mainly of water and CO<sub>2</sub>. Therefore, the content of water in mantle minerals and rocks attracted great attention. The hydrous minerals in the mantle includes amphibole, phlogopite and the  $\alpha$ - and  $\beta$ -phase in the MgO-SiO<sub>2</sub>-H<sub>2</sub>O system. However, in the nominal anhydrous minerals, such as olivine, garnet, pyroxene, quartz, zircon, rutile, kyanite, sanidine and coesite, as proved by infrared spectroscopy and Raman spectroscopy, the water contained in them occur as OH— an essential structural component. The concentrations of structural OH in mantle minerals range from a few ppm to a thousand ppm. The concentration of OH in mantle rocks is from 28 ppm to 565 ppm. In this situation, we cannot but raise a few problems: how would such a little water be concentrated and lead to mantle metasomatism, and would the water come from a deeper source?

Up to now, the composition of mantle fluid was derived from the mantle-derived rocks, i.e. basalts, kimberlites, lamprotes and their mantle rock inclusions. It is evident that the inclusions in diamond samples would be more nicely conserved than those above samples because of the chemical inert of the diamond, and the diamond perhaps occurs much deeper than the mantle rock inclusions do. Navon *et al.*<sup>[15]</sup> and Ozima *et al.*<sup>[16]</sup> reported the fluid inclusions which occurred in cubic diamonds and coats of coated diamond. Chen *et al.*<sup>[2-4]</sup> discovered the chloride inclusions in octahedral and rhombic dodecahedral diamonds. Schrauder<sup>[17]</sup> and Navon<sup>[15]</sup> discovered the solid carbon dioxide. Zheng *et al.*<sup>[18]</sup> observed the fluid inclusions consisting of water, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, NH<sub>3</sub>, etc. in octahedral and cubic-octahedral diamonds. Xue *et al.*<sup>[19]</sup> discovered hydroxyl in type-I<sub>a</sub> diamond.

According to the growth depth of diamond, it may be seen that water and CO<sub>2</sub>

associated with cubic and coated diamonds are characteristic of diamond growing at shallow levels. The hydroxyl related to type-I<sub>b</sub> diamonds reflects the moderate-deep occurrence of diamonds and molecular hydrogen is characteristic of much deeper occurrence of diamonds.

Then we can establish a model for hydrogen action in deep earth. The hydrogen in the earth core is transported through the core-mantle boundary upwards with heat. The ascending hydrogen with oxygen in the mineral lattice experienced chemical reaction producing hydroxyl, and followed by hydrogenation into water. The hydrogen and its hydrogenation products could account for the change of mantle fluids at different earth depths, and describe the main mass transport in mantle plumes.

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