

High-Resolution Stimulated Raman Gain Spectroscopy of Parahydrogen Crystals

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High-resolution stimulated Raman gain spectroscopy of the $Q_1(0)$ transition of para- H_2 crystals with varying ortho- H_2 concentrations is reported. A crystal containing 0.06% of ortho- H_2 showed a single sharp Raman transition with the width of less than 7 MHz. The Raman signal became broader with increasing concentration of ortho- H_2 . At the concentration of 2%, the spectrum splits into a doublet. The components of the doublet have different dependence on the relative polarization of the pump and probe laser radiations. Physical origin of the splitting and the polarization dependence is yet to be understood.

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1. INTRODUCTION

After the pioneering work by Hardy and Berlinsky on high-resolution MW spectroscopy of solid *para*- H_2 ,¹ various infrared transitions of solid H_2 have been studied under high-resolution.²⁻¹¹ The narrowest linewidth so far reported is 4 MHz ($=0.0001\text{ cm}^{-1}$) for the pure vibrational $Q_1(0)$ transition ($v=1 \leftarrow 0, J=0 \leftarrow 0$) of D_2 impurities in a *para*- H_2 crystal.⁵ The sharpness of infrared transition stems from the weak intermolecular interaction and large lattice constant of solid H_2 .¹²⁻¹⁴ The sharp transitions allowed us to obtain detailed information on various interactions and dynamics in solid *para*- H_2 .

In a previous letter, we reported the stimulated Raman gain spectrum of the $Q_1(0)$ transition of a nearly pure *para*-H₂ crystal.¹⁵ The surprisingly small half-width of the observed line was 7 MHz, and it was instrumental limited.

In this paper we report high-resolution stimulated Raman gain spectroscopy of the $Q_1(0)$ transition of *para*-H₂ crystals with various concentrations of *ortho*-H₂. Such experiment was reported using classical Raman spectroscopy by Soots *et al.*,^{18,19} who observed broadening and shift of Raman transitions upon increasing of the concentration of *ortho*-H₂. In order to obtain more precise information on the nature of the $v = 1$ vibron Bloch wave and its scattering process, we have studied the $Q_1(0)$ Raman transition of crystals containing relatively low *ortho*-H₂ concentrations (0.06–2%) by high-resolution stimulated Raman spectroscopy.

2. EXPERIMENTAL DETAILS

The preparation method of a nearly pure *para*-H₂ crystal was the same as reported earlier.^{3,5} In our experiments, H₂ gas was first passed through a chemical purifier (Johnson–Matthey HP-50) and then converted to 99.9% pure *para*-H₂ by passing down a column of APACHI nickel silica catalyst immersed in a liquid H₂ bath. The converted gas was stored in a ballast. The concentration of *ortho*-H₂ was adjusted by mixing *normal*-H₂ into the *para*-H₂ gas in the ballast. Crystals were grown by introducing the mixed gas continuously into a cylindrical copper cell at 7 K. Both ends of the cell were sealed with sapphire windows using indium gaskets. The diameter of the cell was 1.7 cm and the length was 11.5 cm. After the crystal was made, the temperature of the cell was lowered to 4.2 K. Crystals prepared by this method were optically transparent without a crack. Crystals grow radially inward from the cylindrical copper surface. The *c*-axis of the crystal is found to be along the direction of sample growth.⁵

Figure 1 shows schematic diagram of the stimulated Raman gain spectrometer used. A single frequency Ar ion laser (Coherent Innova 90, 488 nm) of 700 mW was used as the pump laser, while a ring dye laser (Coherent 699-21 ring dye laser, 612 nm) of 300 mW was used as the probe. The frequency of the dye laser was scanned and a stimulated Raman signal was detected as an increase of the probe radiation on the detector. For the calibration of the Raman frequency, we observed the infrared absorption lines of CH₄ simultaneously by infrared radiation generated by taking difference frequencies of these two laser radiations with a LiNbO₃ crystal. After the infrared generation, the two visible beams were separated by a dichroic mirror and

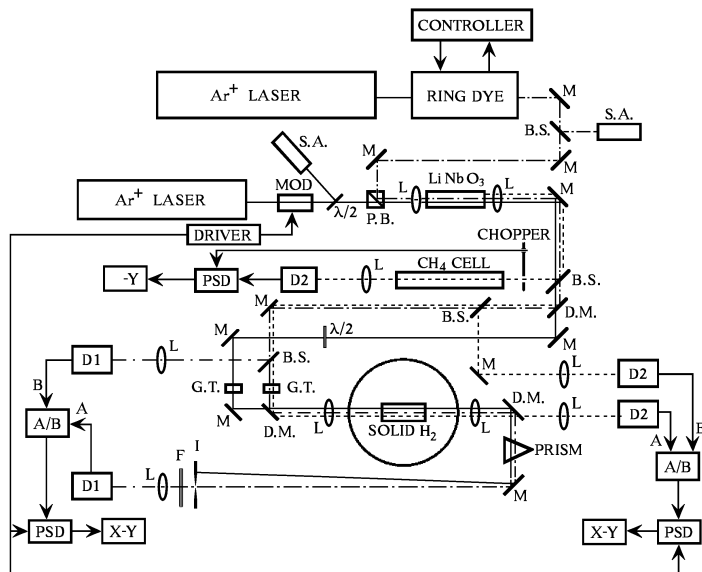


Fig. 1. Experimental arrangement of the stimulated Raman spectroscopy with the infrared generation for the frequency standards. D1 : PIN diode detector, D2 : InSb detector, $\lambda/2$: half-wave plate, B.S. : beam splitter (CaF_2), G.T. : Glan–Taylor polarizer, D.M. : dichroic mirror, P.B. : polarizing beam splitter, S.A. : spectrum analyzer, F : filter, I : iris, MOD : modulator (chopper or KDP crystal), PSD : phase sensitive detector, A/B : divider. Solid line : 488 nm radiation, broken line : 612 nm radiation, dotted line : IR radiation.

their polarizations were rotated independently using Glan–Taylor polarizers. Then the two beams were collimated again and focused into the crystal with a lens of $f = 250$ mm. After passing through the crystal, the two beams were separated by a prism and the change of the intensity of the probe light was detected by a PIN photodiode. In order to compensate the amplitude noise of the probe radiation, power of the probe laser was detected with a separate photodiode to normalize the Raman signal.

3. STIMULATED RAMAN GAIN SPECTRUM

The $Q_1(0)$ stimulated Raman signal of the nearly pure *para*-H₂ crystal (99.90% *para*, 0.06% *ortho*, 0.04% residual HD) was reported previously.¹⁵ The half-width of the signal was 7 MHz, which is close to the spectral purity of the Ar ion laser we used. The intrinsic half width is thought to be much

less than 7 MHz. The spectral line was single with no hint of asymmetry or splitting.

The sharpness of the Raman spectrum is a result of the exciton momentum selection rule, $\Delta k = 0$. The $v = 1$ excited state in solid *para*-H₂ is completely delocalized in the crystal, which is often referred as a vibron.^{12,13} Due to intermolecular interaction, the $v = 1$ state of solid H₂ forms a band with the bandwidth of about 4 cm⁻¹. Each level in the band is labeled by the exciton (vibron) momentum quantum number k . In *para*-H₂ with hcp lattice, only one level in vibron band is Raman active, the $k = 0_+$ state located at the lowest end of the band.¹³ This selection rule is called the exciton momentum selection rule, or the $\Delta k = 0$ selection rule. The sharpness of the observed $Q_1(0)$ Raman signal demonstrates that the selection rule is strict for crystals of nearly pure *para*-H₂.

Raman gain G_R of the stimulated Raman process under the weak field approximation in the *cgs* units is expressed as follows:²⁰

$$G_R L = \frac{16\pi^3 \omega_s N}{hc^2 \Gamma} \alpha_R^2 I_P, \quad (1)$$

where N is the number density of the material (2.64×10^{22} particle·cm⁻³ for a *para*-H₂ crystal at 4.2 K,¹³) ω_s is the wavenumber of the probe laser (1.6×10^4 cm⁻¹), c is the speed of light, h is the Planck constant, Γ is the half width of the signal (0.0002 cm⁻¹), α_R is the Raman polarizability (1.1×10^{-25} cm³ for gaseous H₂,²¹), I_P is the pump laser power (100 W cm⁻²), and L is the length of the sample (11.5 cm). The observed Raman gain was on the same order of magnitude as the estimated values of 5×10^{-3} from the above equation.

Since two laser radiations were used for the stimulated Raman gain spectroscopy, the signal is expected to depend on the orientation of the polarization of each radiation, as well as on the orientation with respect to the crystal axis. For the $Q_1(0)$ spectrum, however, the signal is independent of the crystal orientation. When the polarization of two laser radiations were parallel to each other, the Raman signal was the strongest, and when the polarizations were perpendicular to each other, no signal was observed, irrespective of the orientation of the crystal axis. The polarization dependence is reasonable since the $Q_1(0)$ Raman transition occurs through the isotropic polarizability of the $J=0$ H₂, hence no perpendicular transition is allowed.

The shape of the signal was very sensitive to the condition of the crystal. When we focused the pump beam tightly into the solid and left it for several hours, the Raman signal became asymmetric and the width became more than twice as broad as the initial signal. When we changed the focal point, a sharp single line was again observed. This fact indicates that a part of

the crystal was damaged by the strong laser radiation, and the damage in the crystal induced scattering of the $\nu = 1$ Bloch wave resulting in the deformation of the Raman spectrum.

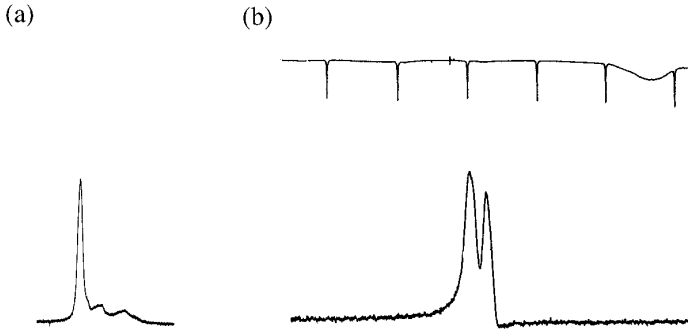


Fig. 2. The $Q_1(0)$ stimulated Raman signal of a $para$ -H₂ crystal with $ortho$ -H₂ concentration of (a) 0.2% and (b) 2%. Top trace in (b) is the signal from a spectrum analyzer with FSR = 1500 MHz. The Raman frequency increases from the right to left.

Figure 2 shows the stimulated Raman spectra of the solid H₂ with different $ortho$ -H₂ concentrations. The trace (a) shows the spectrum of a $para$ -H₂ crystal with 0.2% $ortho$ -H₂ concentration and the trace (b) shows that of a crystal with 2.0% $ortho$ -H₂. In Figure 2a, there are one intense peak at higher frequency and three weak peaks at lower frequency. The calibrated frequency of the strongest line was 4149.699 cm^{-1} . The half-width of the signal was about 32 MHz. The frequency shifts of the weak peaks from the strongest signal are about -160 MHz , -380 MHz , and -580 MHz , respectively. On the other hand, as shown in Figure 2b, the signal of the crystal with 2.0% $ortho$ -H₂ concentration has two peaks with almost equal intensity. The separation of the peaks was about 300 MHz. The frequency of the higher frequency signal was 4149.762 cm^{-1} and its half-width was about 150 MHz.

When the concentration of $ortho$ -H₂ was increased, the signal shifted to higher frequency and became broader. The frequency shift is caused by the change of the band width of the $\nu = 1$ vibron in the solid by the existence of increased $ortho$ -H₂. Since the interaction between $para$ -H₂ and $ortho$ -H₂ is slightly stronger than the interaction between two $para$ -H₂, the bandwidth of the $\nu=1$ vibron must be changed by the existence of impurities. The fact that the Raman signal was shifted to higher frequency indicates that the bottom end of the band corresponding to the $k = 0_+$ state is pushed up by the existence of $ortho$ -H₂ impurities. Soots *et al.*^{18,19} found that the shift

of the $Q_1(0)$ line depends linearly on the concentration ratio of *ortho*- and *para*-H₂. If we apply their empirical equation for the cases of 0.2% and 2% *ortho*-H₂ concentrations, the frequency shift calculated is about 0.05 cm⁻¹, close to our observed shift of 0.06 cm⁻¹.

The broadening of the spectrum upon increasing the *ortho*-H₂ concentration can be explained as the mixing of $k \neq 0$ states into the $k = 0$ state due to the presence of *ortho*-H₂. In other words, due to the mixing of different k states, the vibron is partially localized in the solid, which cause the breakdown of the momentum selection rule $\Delta k = 0$. The weak sidebands observed for 0.2% *ortho*-H₂ concentration must be a result of the mixing of different k states.

The size of vibron at various *ortho*-H₂ concentration can be estimated from the broadening of the signal by the use of the effective mass approximation.¹² According to that approximation, which is known to be a good approximation for small k , the dispersion relation can be written as

$$E_R = -7.23\varepsilon + \frac{\hbar^2 k^2}{2M}, \quad (2)$$

where M is the effective mass of the vibron and ε is the interaction matrix element. Using the Heisenberg uncertainty principle, the relation between the energy uncertainty ΔE and the size of the exciton R can be expressed as

$$\Delta E = \frac{\hbar^2}{2MR^2}. \quad (3)$$

The finite size of the exciton of $R = 8R_0$, $16R_0$, and $24R_0$, where R_0 is the intermolecular distance in the crystal ($R_0 = 3.783 \text{ \AA}$), give the energy uncertainty of 160 MHz, 40 MHz, and 15 MHz, respectively. These uncertainties are considerable compared to that we observed in the crystals of 2%, 0.2%, and 0.06% *ortho*-H₂, respectively. Perhaps, these numbers can be considered to be the effective size of vibron at each *ortho*-H₂ concentration.

However, the doublet observed in the crystal containing 2% *ortho*-H₂ cannot be explained by the mixing of different k states. Figure 3 shows the polarization dependence of the doublet of the 2% crystal. Figure 3a shows the spectrum when the polarizations of the two laser radiations were parallel, whereas Figure 3b shows the spectrum when the polarizations were perpendicular to each other. It is clear that the signal at lower frequency was stronger for perpendicular configuration. The polarization dependence cannot be explained by considering only the $J = 0$ state in the solid, because the stimulated Raman transition with vertical polarization occurs through the anisotropic polarizability of H₂, however the $J = 0$ state is completely isotropic. Possible explanation is the mixing of the $J = 2$ state into the $J = 0$

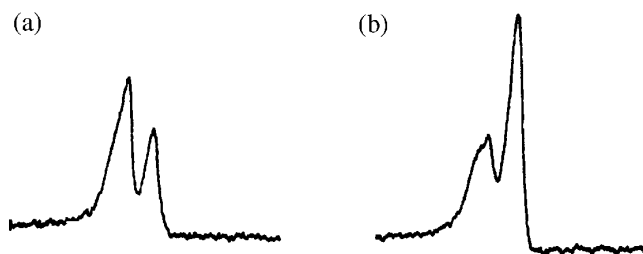


Fig. 3. Polarization dependence of the $Q_1(0)$ signal of a $para$ -H₂ crystal with 2% $ortho$ -H₂ concentration. (a) Polarizations of two laser radiation are parallel. (b) Polarizations of two laser radiation are perpendicular.

state due to the existence of $J=1$ H₂. The mixing is caused by the second order EQQ interactions.¹³ Once the the $J=2$ state mixes into the $J=0$ state, the $J=0$ H₂ has nonzero anisotropic polarizability which makes the Raman transition with vertical polarization possible. However, this model still does not explain the strong intensity of vertical component shown in Figure 3, since the mixing must be small due to the large energy difference between the $J=0$ and $J=2$ states, and hence it does not induce such a strong Raman signal for the vertical component even at the 2% crystal.

The physical origin of the splitting and the polarization dependence of the $Q_1(0)$ transition doublet at relatively high $ortho$ -H₂ concentration is still not clear and needs further discussion. The experimental data is very clear and reproducible, it may contain new physical phenomena related to the scattering of Bloch waves in crystals. Further study is needed.

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