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Vibrational and Rotational Raman Spectra of Trapped Hydrogen in Irradiated Ethanol Crystal at 77 K

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Synopsis. Trapped hydrogen molecules were produced in γ-irradiated ethanol crystal at 77 K and their Raman spectra of Q- and S-branches were observed at 77 K for the first time. Relative scattering intensities of the bands due to p-H_2 (Q_1 (0), S_0 (0)) and o-H_2 (Q_1(1)), S_0(1)) were measured and compared with the reported results of solid normal hydrogen.

Recently we have reported[1] Raman spectra of trapped hydrogen produced in γ-irradiated ethanol glass and crystal at 77 K. The spectral feature of the vibrational bands (Q-branch) showed: (1) the band maximum at 4133 (20), 4155 (10) cm^{-1} for glass and crystal, respectively, where numbers in parentheses are full width at half maximum (FWHM), (2) the contour fitting Gaussian for glass, while Lorentzian for crystal, (3) the integrated intensity being same for glass and crystal.

In this study we have observed two peaks in the Q-branch spectrum and two separate bands of the S-branch of trapped hydrogen produced in γ-irradiated ethanol crystal at 77 K.

Ethanol crystal samples of 0.4 cm in thickness and 2 cm in diameter were made as described previously.[1,2] Irradiation with γ-rays was carried out at 77 K and the total dose was 1130 kGy. Raman spectra were measured at 77 K with a JASCO NR1100 spectrometer. The 514.5 nm line of Ar ion laser (NEC) with a typical output of 800 mW was used as an excitation source.

The profile of the Raman bands due to the Q- and S-branches of hydrogen is shown in Fig. 1, A, and B, respectively. In the Q-branch spectrum, two peaks at 4153 and 4159 cm^{-1} are distinguished. These peak wavenumbers are in good accordance with those due to compressed gaseous normal hydrogen, i.e. 4153 and 4158 cm^{-1} at 398 Amagat at 87 K,[3] but shift to high frequencies by about 7—10 cm^{-1} from those of solid normal hydrogen at 2 K.[4] These peaks were ascribed to Q_1 (1) ($\Delta v=1$, $\Delta J=1$) and Q_1 (0) ($\Delta v=1$, $\Delta J=0$) transition, respectively.[3-5] Note that Q_1 (0) transition is characteristic of parahydrogen (p-H_2), while Q_1 (1) of orthohydrogen (o-H_2). For irradiated ethanol glass, the vibrational band (Q-branch) of hydrogen is structureless and broader (FWHM=17 cm^{-1}) compared to that for the crystal.[1] The observed Q-branch spectrum for the crystal can be resolved into two Lorentzian bands at 4153 (6) and 4159 (3.5) cm^{-1} with their intensity ratio of 3, where the numbers in parentheses are FWHM values. On the other hand, the intensity ratio of the corresponding bands in solid normal hydrogen at 2 K[4] is estimated to be about 15.

In the S-branch spectrum two bands appear at 358 and 590 cm^{-1}. These peak wavenumbers are very compatible to those for compressed gaseous normal hydrogen (355 and 588 cm^{-1})[5] and also those for solid normal hydrogen (351 and 587 cm^{-1}).[4] The 358 cm^{-1} band was ascribed to S_0 (0) ($\Delta v=0$, $\Delta J=2$) transition and the 590 cm^{-1} band to S_0 (1) transition.[3-5] It should be cited that S_0 (0) branch appears in p-H_2 while S_0 (1) does in o-H_2. The observed bands of the S-branch fit Lorentzian at 590 (8) and 358 (8) cm^{-1} with their intensity ratio of 0.5. Note that this value is much smaller than

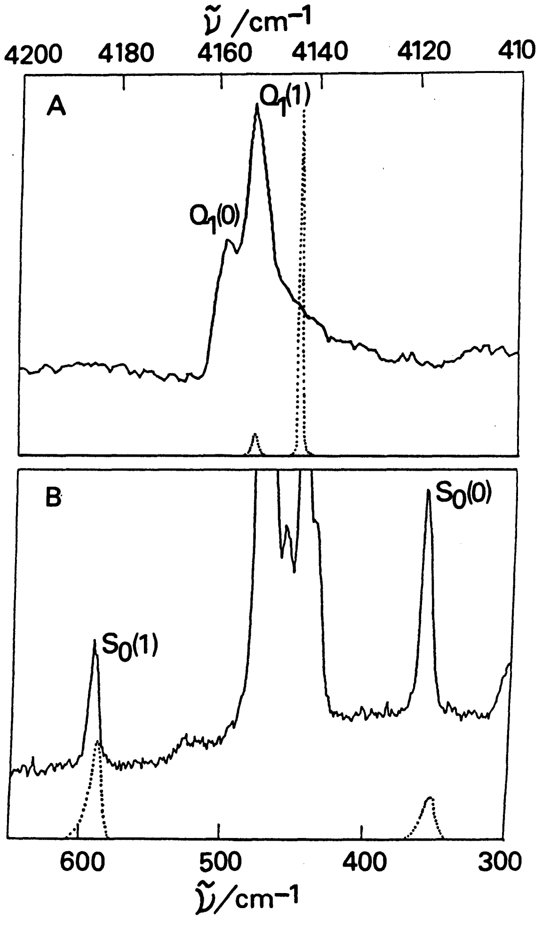

Fig. 1. The Raman spectra of trapped hydrogen in irradiated ethanol crystal at 77 K. The sample was irradiated by γ-rays at 77 K and the dose was 1130 kGy. Raman spectra were measured at 77 K; (A) H_2 vibrational band, and (B) H_2 rotational bands. The intense bands between ca. 420 and 470 cm^{-1} are due to intramolecular modes of ethanol molecule including CCO bending. The dotted spectra are reproduced ones for solid normal hydrogen at 2 K (after Bhatnagar et al. 1962).[4]

those estimated for solid normal hydrogen, i.e. 2,[4] or normal hydrogen dissolved in ice, i.e. 3.[6]

It is concluded from the intensity ratios of the Q- and S-branches that the relative concentration of p-H_2 in irradiated ethanol is much larger than the relative concentration of p-H_2 in solid normal hydrogen at low temperatures. There are three possible explanations for the phenomenon: (1) a selectivity of the rotational quantum state for hydrogen formation by radiolysis of alcohol at low temperatures, (2) an exchange reaction of $H+o\text{-}H_2 \rightarrow H+p\text{-}H_2$ caused by the hydrogen atoms[7] which are produced during the radiolysis, and (3) the conversion from $J=1$ to $J=0$ states during storage of the irradiated sample in liquid nitrogen, that is a thermal equilibrium.

Further study is in progress to elucidate the mechanism.

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