

12. Structural Changes of Organic Solids Caused by Irradiation: Raman Study at Very Low Temperatures.

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I INTRODUCTION

Upon irradiation of organic solids, a variety of ionic species, free radicals and molecular products is generated and some of them are stably trapped in matrices at low temperatures and are normally detected by ESR and optically spectroscopic methods. However, molecular products trapped in low temperature matrices are scarcely detected, since they are neither paramagnetic nor uv-vis (250-800 nm) absorbing species. We have been aware of the utility of Raman spectroscopy for detecting molecular products as well as ionic species and free radicals, since most of them are Raman active. We have also realized that this method can shed light on structural changes caused in irradiated organic solids by observing spectral changes in intra- and intermolecular vibration modes.

It is instructive to note that the vibrational modes of a disordered medium obey Bose-Einstein statistics, so that the correction for the observed Raman spectra is usually made with use of the so called Bose-Einstein factor, $f_{BE} = \{1 - \exp(h\nu/kT)\}^{-1}$, where ν is the Raman shift in wavenumber and T is the temperature of the sample. The factor depends on both frequency and temperature, e.g. at 77 K $f_{BE} = 0.372$ and 0.976 at 25 and 200 cm^{-1} , respectively, but becomes independent of frequency at very low temperatures, i.e. $f_{BE} = 1.00$ for all frequencies at 5 K. This convinces one that Raman spectroscopy at very low temperatures is indispensable for measurement of organic solid, particularly in the low frequency region.

In reality, however, the focusing of an intense laser beam on the surface of a sample causes a considerable rise of the local temperature. This makes Raman scattering measurements at low temperatures very difficult if the sample is mounted in a conventional conduction-

tail cryostat. Furthermore, this type of cryostat is not suitable for organic glass samples because mounting and handling of the glass samples without warming are required, otherwise the samples often change their thermodynamical properties or melt above certain temperatures.

Another type of cryostat is a flow-gas helium cryostat in which cold helium gas flows down, being directed onto the sample surface^{1,2}). This type of cryostat may be more efficient for preventing the temperature rise of the sample than a conduction-tail cryostat, but still being not satisfactory for organic glass samples because of the difficulties mentioned above. Recently Weng *et al.*³) reported Raman spectra of ethanol and deuterated ethanol glasses as a function of temperature above about 10 K with a flow-gas helium cryostat. This temperature is the lowest one reported for alcohols as far as we are aware.

In this paper we first describe a simple liquid helium cryostat and a device of making and mounting organic solid samples. We then present the Raman spectra for irradiated ethanol crystal that were obtained by using the new cryostat and demonstrate how the Raman method is useful for getting insight into structural changes of organic solids caused by irradiation.

II APPARATUS

The cryostat is made of an inner quartz vessel which is fixed in a cylindrical vacuum chamber of thin-walled stainless steel⁴). The details of the cryostat are shown in Fig. 1. A bottom window for the incident laser beam and a side window for the scattered light, both of which are of optical-quality Suprasil quartz, are attached onto the wall of quartz vessel (D), and outside of the vessel was aluminized to reduce radiation losses. The vessel is surrounded by a cylindrical

thin-walled stainless steel reservoir for liquid nitrogen (C). The bottom wall of the reservoir is in thermal contact with a copper radiation shield boot (G) which has holes for the optical windows (K). Vessel D and bath C hold 1.8 and 1.5 ℓ of liquid helium and liquid nitrogen, respectively, which enable us to carry out measurements for 2.5h under the irradiation of a typical Ar ion laser beam of 1.5W of the maximum output onto the organic solid samples through the bottom optical window.

The temperature of the organic solid samples under the irradiation of the laser beam of 1.5W was measured by a Au + 0.07% Fe vs. Cr thermocouple which was shallowly inserted in the organic solid samples at the irradiation point of the laser beam. Any change of the thermoelectric voltages on the irradiation of the laser beam was not detectable in the range of $5\mu\text{V}$ in liquid nitrogen. The difference in liquid helium was not more than $10\mu\text{V}$. This indicates that the temperature of the sample does not exceed 5 K in liquid helium under the irradiation of the laser beam.

Another feature of the cryostat is worthy to note. If one wants to use the cryostat as a conduction-tail cryostat, the inner quartz vessel can be replaced by a conduction-tail vessel which is made of a thin-walled stainless steel with a copper conduction tail. A sample dish, which will be described later, is screwed into the top of the conduction tail and can be easily changed by removing flange H out of chamber B.

Disk samples of organic solids with a thickness of 0.4 cm and a diameter of 2 cm were made by dropping drops of solution on brass dishes which were kept at liquid nitrogen temperature. The cross-sectional view of the sample dish is shown in the insert of Fig. 1.

The sample making procedure is similar to the one reported previously⁵⁾ except for the brass dish employed in this apparatus instead of a washer-like brass ring. The sample dish is screwed into the stainless steel joint at the top of the glass fiber holder as shown in the insert of Fig. 1. The length of the holder and the angle of incidence of the reflected light to the optical window can be changed by turning a nut (A) outside the cryostat so that the maximum intensity of Raman scattering can be obtained.

It is worthy to note that the present cryostat has a remarkable advantage when it is used at liquid nitrogen temperature.

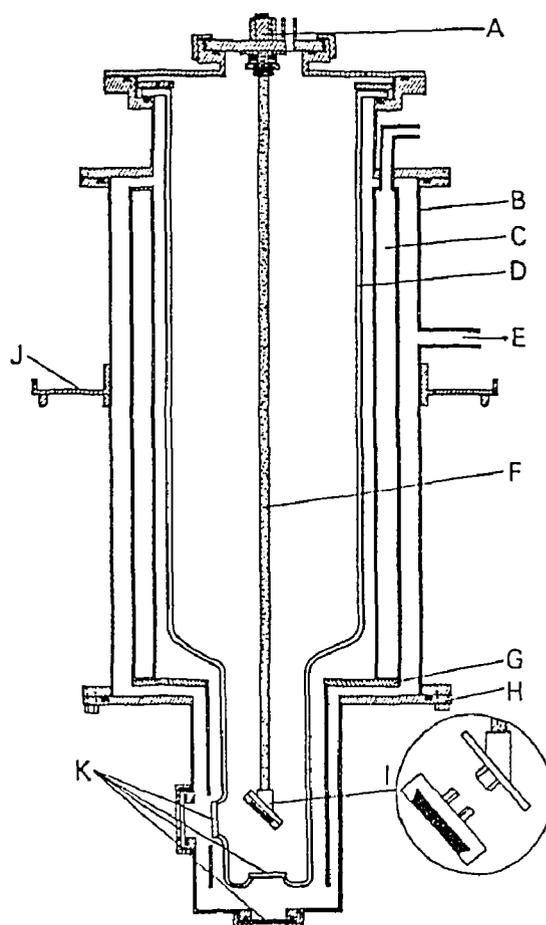


Fig.1 Cross-sectional view of the cryostat for Raman spectroscopy. A-Nut for adjusting the length of the glass fiber sample holder and changing the angle of incidence of the reflected light to the optical window; B-Thin-walled stainless steel cylinder of 15.5 cm i.d.; C-Stainless steel nitrogen reservoir; D-Quartz vessel of 9.6 cm i.d. for liquid helium; E-Vacuum pumping port; F-Glass fiber sample holder; G-Copper radiation shield boot; H-Removable flange; I-Brass sample dish and holder; J-Support flange; K-Optical quality window of Suprasil quartz.

It has been commonly recognized that the measurement of Raman scattering of samples inserted in liquid nitrogen is difficult because of the noise caused by irregular bubbles passing across the scattered light. With the present cryostat, however, no bubbles occur in liquid nitrogen of the inner vessel when the outer nitrogen bath is filled with liquid nitrogen. This allows us to measure Raman spectra with extremely reduced noise at liquid nitrogen temperature.

III EXPERIMENTAL

Regent grade ethanol was used without further purification. Ethanol crystal was prepared by annealing ethanol glass near the melting point for 40 min according to the recipe of Jönsson⁶⁾. Irradiation with γ -rays was carried out at liquid nitrogen temperature. The total dose was 1130 kGy for ethanol crystal. The temperature of the disk samples in liquid helium did not exceed 5 K during the exposure to the laser beam of ~ 800 mW by the 514.5 nm line of a NEC argon-ion laser as an exciting source. Raman spectra were recorded with a JASCO NR-1100 spectrometer. The CCO symmetric stretching band of ethanol crystal at 891 cm^{-1} was used as an internal standard, on the basis of the assumption that the intensity of the skeletal stretching is hardly affected by the transformation of an ethanol molecule into an ion or a radical. In fact, Edwards *et al.*⁷⁾ showed evidence for the suitability of CCO stretching band as an internal standard of ethanol. Thus the relative intensities of the Raman bands before and after irradiation were determined respectively, and the intensity ratio was determined between them.

IV RESULTS AND DISCUSSION

Intermolecular vibration region

In the wavenumber region below 300 cm^{-1} of the ethanol crystal, the intermolecular vibration modes as well as the hydrogen bond stretching mode were observed⁸⁾. This shown in Fig. 2.A. The spectra observed are in good accordance with those reported by Weng *et al.*³⁾. Assignment of peaks seems to be difficult, since the spectra are too complicated to be resolved and also some mixing of modes might be occurred. Weng *et al.*³⁾ tried to assign the peaks by examining the frequency ratios for ethanol and deuterated ethanol and comparing them with the inertia ratios. According to their results, the peaks observed at 66, 89, 102 and 137 cm^{-1} are attributed to the translation, while the peaks at 56 and $120\text{--}126\text{ cm}^{-1}$ are attributed to the libration. We ascribe the band at 294 cm^{-1} to the hydrogen bond stretching as described previously⁹⁾.

After irradiation at 77 K, the intermolecular bands showed the drastic changes. This is demonstrated in Fig. 2B. It follows that the translation peaks shift towards the low wavenumber side by about 10 cm^{-1} , and increase in

their intensities. The libration peaks, on the other hand, neither shift nor increase in the intensities.

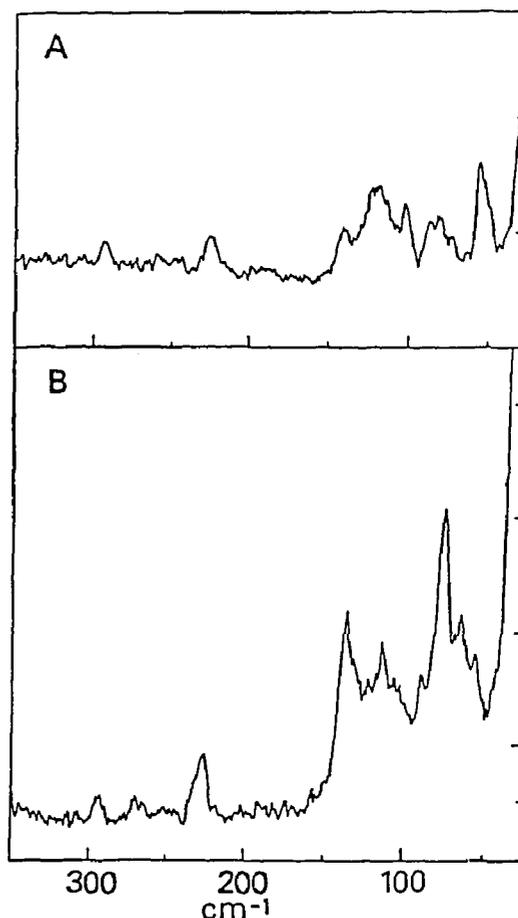


Fig.2 Raman spectra of ethanol crystal in the wavenumber region of the intermolecular vibration modes. The spectra were measured before(A) and after(B) irradiation at 77 K. The total dose was 1960 kGy.

It is inferred that some structural changes occur in such a way that freedom of the initial translational vibration is reduced, but that the population of the translational vibration is enhanced. We infer that radiation-produced species which are trapped in the interstitial sites of the crystal form additive hydrogen bondings to a chain of ethanol molecules. A most probable candidate of the species is hydrogen molecules. In fact the hydrogen bond stretching band at 294 cm^{-1} increased in intensity by about 30 % after irradiation.

Intramolecular bending region

The intense intramolecular modes including the CCO bending of ethanol molecules appear in the wavenumber region of $420\text{--}470\text{ cm}^{-1}$, as shown in Fig. 3A. After irradiation at 77 K, a set of sharp bands was observed at 358 and 590

cm^{-1} 10). This is shown in Fig. 3B.

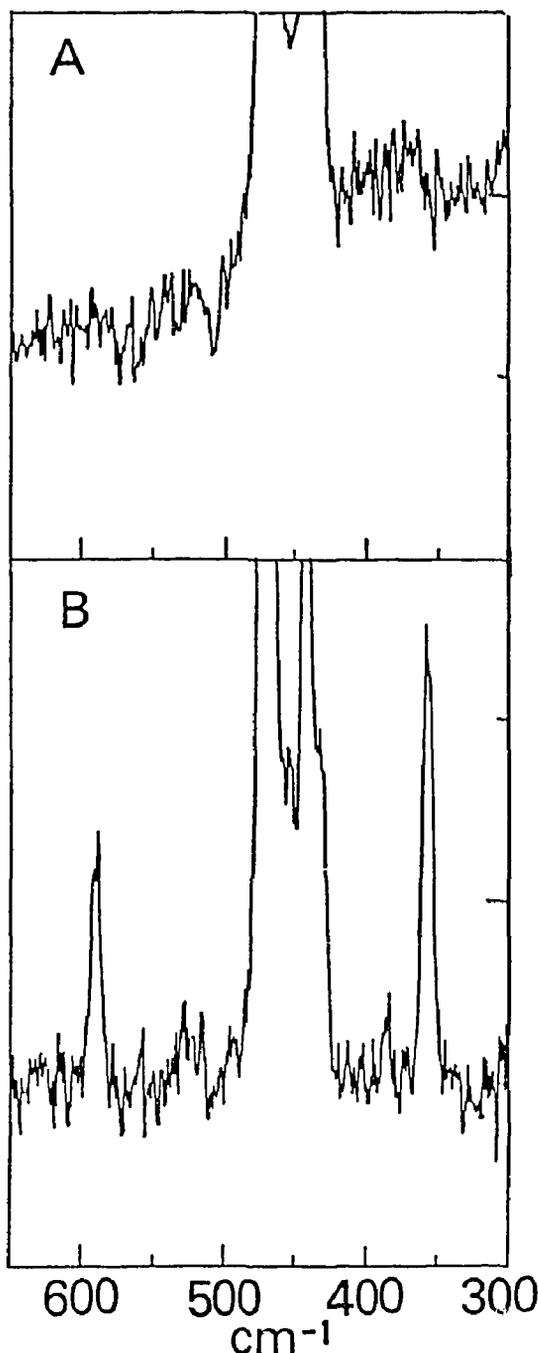


Fig.3 Raman spectra of ethanol crystal in the wavenumber region of intramolecular bending modes at 5 K. The spectra were measured before(A) and after(B) irradiation at 77 K. The total dose was 1130 kGy. The intense bands at 420-470 cm^{-1} are attributed to the intramolecular modes including CCO bending of ethanol molecules.

The wavenumbers observed are very compatible to those for compressed gaseous normal hydrogen, that is 355 and 588 cm^{-1} 11), and also those for solid normal hydrogen, that is

351 and 587 cm^{-1} 12). These are assigned to the rotational bands of hydrogen molecules: The 358 cm^{-1} band is ascribed to $S_0(0)$ ($\Delta v=0$, $\Delta J=2$) transition and the 590 cm^{-1} band to $S_0(1)$ transition. We emphasize that this is the first and direct evidence that hydrogen molecules are produced and trapped in irradiated ethanol crystal.

It was well known at a quarter of a century before that a large yield, i.e. $G(\text{H}_2)=5$ of gaseous hydrogen is observed after melting solid ethanol which was previously irradiated at 77 K^{13,14}). It was assumed that hydrogen atoms, which are not stably trapped in alcoholic solids, undergo the reaction of hydrogen molecule formation. The reaction was thought to occur through a tunneling abstraction at cryogenic temperatures such as 4 K.

Although there is convincing, indirect evidence that hydrogen molecules are formed in irradiated alcoholic solids at cryogenic temperatures, no direct observation of hydrogen molecules in solids has been reported so far. Since hydrogen molecules absorb light of the near u.v. region in the gas phase, it is almost impossible to apply ordinary optical absorption methods to detecting hydrogen molecules in alcoholic solids at cryogenic temperatures. Considering that hydrogen molecules are not infra-red active, but are Raman active, we can apply Raman spectroscopy as the unique, experimental technique to directly detect hydrogen molecules which are produced by irradiation and are trapped in solids. We have now demonstrated that this is the case.

OH stretching region

Shown in Fig. 4A is the OH stretching bands of ethanol crystal obtained at 5 K before irradiation. It is noted that the OH stretching bands of the crystal differ from those of glass. The former consists of two bands at 3144 and 3260 cm^{-1} and a small band at 3229 cm^{-1} and their contours fit Lorentzian, while those of glass fit Gaussian. Comparison of the spectral profiles of crystal and glass leads us to the conclusion that the hydrogen bond networks in the crystal are distinctly classified into two configurations, and that they are strengthened and homogenized much more than in glass. It is known from the X-ray work of Jönsson⁶) that the infinite zigzag chain is formed through the hydrogen bond in ethanol crystal and that two kinds of hydrogen bond exist with the distance

of 2.716 and 2.730 Å. Recalling that the hydrogen bond distance of 0.014 Å yields a separation of 75 cm^{-1} ¹⁵⁾, we attribute the bands at 3144 and 3260 cm^{-1} to OH stretching associated with short and long hydrogen bond, respectively. The small band at 3229 cm^{-1} might be due to a distribution of hydrogen bond length in consequence of a disordered configuration in the crystal.

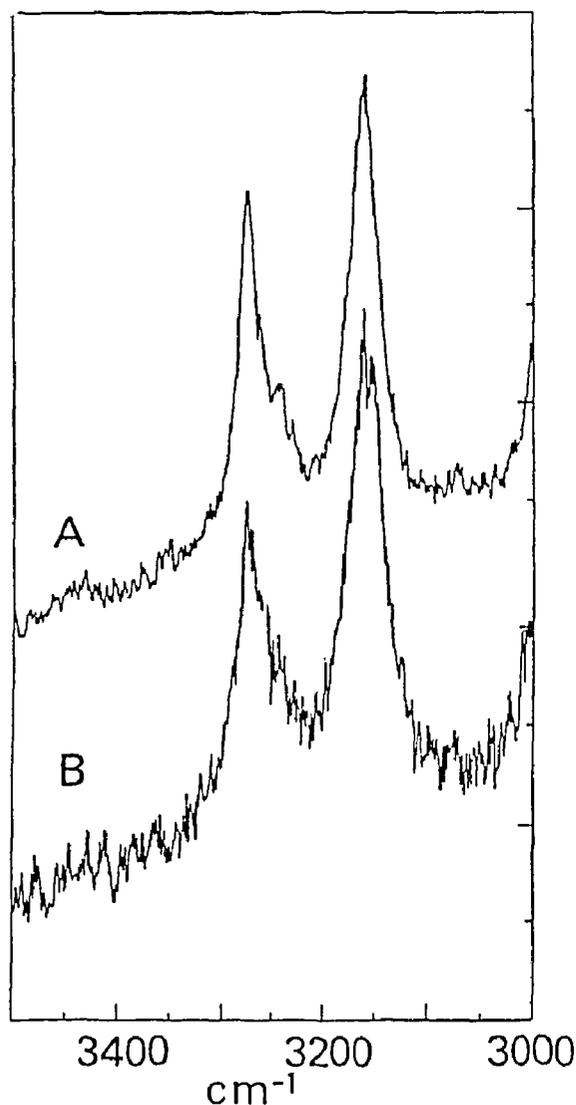


Fig.4 Raman spectra of ethanol crystal in the wavenumber region of the OH stretching modes at 5 K. The spectra were measured before(A) and after(B) irradiation at 77 K. The total dose was 1130 kGy.

After irradiation, the two main bands shifted slightly toward the high frequency, *ca* 5 cm^{-1} , but the shift of the 3225 cm^{-1} band is, if any, obscure¹⁰⁾. This is shown in Fig. 4B. Note that after irradiation the 3260 band decreases while the 3144 cm^{-1} band increases in the intensity.

The decrease of the weakly hydrogen-bonded OH oscillator and a concomitant increase of the strongly hydrogen-bonded OH oscillator imply that the intermolecular configuration is changed in such a way that additive intermolecular interaction, i.e. hydrogen bonding, is caused by irradiation. The spectral changes after irradiation observed in the intermolecular vibration region as well as the direct observation of the rotational bands due to hydrogen molecules accommodate the above interpretation.

Hydrogen molecule stretching region

In the wavenumber region greater than that of the OH stretching vibration, no spectrum was observed for ethanol crystal before irradiation, as shown in Fig. 5A. After irradiation the Raman spectra were observed at 4133(20) and 4153(10) cm^{-1} for glass and crystal, respectively, where numbers in parentheses are the values of FWHM^{10, 16)}. The spectrum for ethanol crystal provides a sub-band at 4159 cm^{-1} as shown in Fig. 5B. These peak wavenumbers are in good accordance with those of normal hydrogen compressed at 398 Amagat at 87 K¹¹⁾ i.e. 4153 and 4158 cm^{-1} , but shift to the high frequency side by about 8 cm^{-1} from those of solid normal hydrogen at 2 K¹²⁾. 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. It should be noted that $Q_1(0)$ transition is characteristic of parahydrogen (*p*-H₂), while $Q_1(0)$ transition of orthohydrogen (*o*-H₂). The observed Q-branch spectrum for irradiated ethanol 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. This ratio is much smaller than that for solid normal hydrogen at 2 K which is about 15.

It follows that the relative concentration of *p*-H₂ in irradiated ethanol is much larger than that for solid normal hydrogen at 2 K. At present three explanations are possible for the phenomenon: (1) a selectivity of the rotational quantum state for hydrogen molecule formation by radiolysis at low temperatures, (2) an exchange reaction of $\text{H} + \text{o-H}_2 \rightarrow \text{H} + \text{p-H}_2$ caused by H atoms which are produced during radiolysis and (3) the conversion from $J=1$ to $J=0$ states during irradiation and storage of the sample at 77K. Further study should be carried out to elucidate the mechanism.

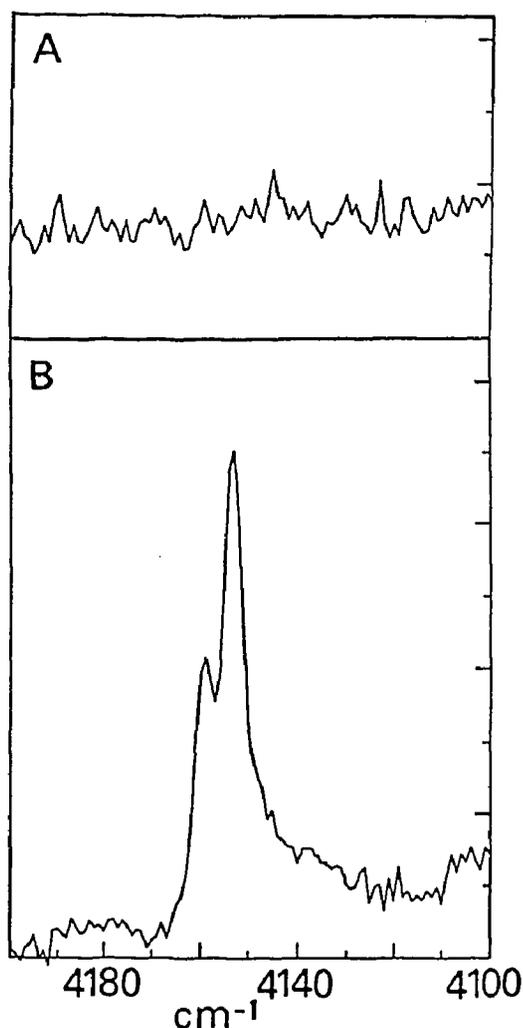


Fig.5 Raman spectra of ethanol crystal in the wavenumber region of the HH stretching of hydrogen molecules at 5 K. The spectra were measured before(A) and after(B) irradiation at 77 K. The total dose was 1130 kGy.

V CONCLUSION

We made a simple but very convenient cryostat for Raman scattering measurement at very low temperatures and used it for investigation of structural changes in ethanol crystal which were induced by irradiation.

The intermolecular vibration modes were affected by irradiation: translation modes enhanced and shifted to the low wavenumber side. This was tentatively interpreted in terms of additional hydrogen bonds formed between the hydroxyl groups and hydrogen molecules, the

latter of which was produced by irradiation. The direct observation of hydrogen molecules produced and trapped in ethanol crystal was first successful in the measurements of the rotational and stretching modes. We emphasize from these results that the Raman scattering measurement at low temperatures is one of the most elegant, efficient techniques to investigate structural changes in organic solids which are induced by irradiation.

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