Raman study on hydrogen bond material 5-bromo-9-hydroxyphenalenone

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Abstract. Raman studies were performed on 0-dimensional hydrogen bond system crystalline 5-bromo-9-hydroxyphenalenone and its deuterated material 5-bromo-9-deuteroxyphenalenone at 40 K. In the former, four Raman peaks which the latter lack were observed at 593, 625, 651 and 1198 cm\(^{-1}\). Since their molecular structures are the same except for the hydrogen bond part, the appearance of additional peaks suggests a possibility that the origins of these peaks are intra-molecule phonons coupled with proton tunnelling motion.

1. Introduction

To study hydrogen bond is very important for many scientists including physicist, chemist and biologist. One of the most interesting phenomena in hydrogen bonded ferroelectric materials is the fact that the ferroelectric-paraelectric transition temperature of the deuterated material is often far higher (for example, more than 100 K) than that of the hydrogen material (sometimes called “giant isotope effect”). There are two types of dielectric phase transition: (1) the order-disorder transition of the permanent dipoles and (2) the appearance-disappearance transition of the dipoles due to the deformation of molecular units (called displacive type). Blinc proposed the proton tunnelling model [1]: The ferroelectricity comes from the local electric dipole generated by the proton pinning to one side of a double minimum potential and the proton tunnelling between the minima destroys the dipole (i.e. the transition is displacive one). As the tunnelling probability has a great mass dependence, the destruction of the dipole occurs strongly in hydrogen materials rather than deuterated ones. However, in spite of huge numbers of studies, the isotope effect has not been clarified fully until now. In most of the hydrogen-bonded ferroelectric systems, the protons tie molecule units and form the inter-molecular hydrogen bond network that is a proton is not only one of the origins of the local dipole but also a connector between the electric dipoles or molecule units, which makes difficult to clarify the role of proton in phase transition. The study must be done in simple systems.

It is known that a 5-bromo-9-hydroxyphenalenone (C\(_{13}\)H\(_6\)BrOOH; call BHP) molecule has an isolated intra-molecule hydrogen bond (figure 1) and has no hydrogen network (zero-dimensional hydrogen bond system) [2].
Moritomo et al. [3] observed an incommensurate transition at 37 K and a lock-in transition at 20 K in BHP, on the other hand no transition was detected in its deuterated molecule C_{13}H_{6}BrOOD (call BDP), i.e. it was shown that the giant isotope effect on phase transition occurs also in no hydrogen network system. Furthermore Matsuo et al. showed that there is an extra degree of freedom in BHP which BDP lacks [4] and observed an absorption peak in BHP around 85 cm\(^{-1}\) at low temperature [5]. This absorption peak was not observed in BDP and therefore attributed to a transition from the ground state to the excited state of a tunnelling proton in a double-well potential located between two oxygen atoms. These results suggest that the phase transition in BHP-BDP system may be dominated by the proton tunnelling and we can study the role of proton tunnelling in the phase transition without any disturbance by the hydrogen network.

Since the Raman scattering is a good tool to investigate the mechanism of phase transitions, as a first step, we tried to detect the Raman peaks related to proton tunnelling motion in crystalline BHP. In order to assign a Raman peak related with the proton tunnelling, it is the best way to show the lack of correspondent in its deuterated material BDP at the same condition.

2. Experimental

Raman studies were carried out at the forward scattering geometry on BHP and BDP single crystals at 40 K where both of them are paraelectric. The samples were mounted on a diamond heat sink directly without any greases or pastes. The specimen was cooled using an Iwatani CryoMini model CRT-006-0000 cooling system and the temperature was controlled using an Iwatani TCU-4 digital program temperature controller. The 632.8 nm line from a He-Ne laser was used for excitation source to avoid strong photo-luminescence and the scattered light was detected by a Jobin-Yvon triple monochromator T64000 and Jobin-Yvon Spex Spectrum-one CCD (charge coupled device) system.

3. Results and discussion

Figures 2-6 are Raman spectra of BHP and BDP obtained at the intra-molecule vibration region. Most of the Raman peaks in BHP correspond with those of BDP and originated from frame vibration of the BHP or BDP molecules. However, in the former, we can find four unpaired peaks (marked by arrows) at 593, 625, 651 and 1198 cm\(^{-1}\). The appearance of additional peaks suggests the existence of additional degree of freedom of vibration. However since their molecular structures are quite the same, the number of vibration modes must be the same, i.e. the origin of these four peaks are not pure intra-molecular vibration. As mentioned above, there exists a proton tunnelling in BHP and the tunnelling splitting is about 85 cm\(^{-1}\). Therefore these peaks are not due to the transition between tunnelling levels. However it is possible that some frame vibration modes couple with the proton motion, which generates additional Raman peaks in BHP.

Matsuo et al. [5] showed that the full width of the absorption peak due to the proton tunnelling is broader (about 16 cm\(^{-1}\)) than that of the ordinary vibrational transition (ca. 3 cm\(^{-1}\)) and thought that
Figure 2. Raman spectra of BHP and BDP obtained at the region of 420-750 cm\(^{-1}\)

Figure 3. Raman spectra of BHP and BDP obtained at the region of 800-1050 cm\(^{-1}\)

Figure 4. Raman spectra of BHP and BDP obtained at the region of 1100-1300 cm\(^{-1}\)

Figure 5. Raman spectra of BHP and BDP obtained at the region of 1400-1600 cm\(^{-1}\)

Figure 6. Raman spectra of BHP and BDP obtained at the region of 1610-1750 cm\(^{-1}\)
one of the possible origins of the broadening is the fluctuating interaction (electronic or otherwise) due to the protons of neighboring molecules. The interaction is random and fluctuates because the protons in neighboring molecules are tunneling from one minimum to the other on their own hydrogen bonds. If so, the Raman peaks related with the proton motion should be broaden. In present case, the widths of the four characteristic Raman peaks are 7 (593 cm\(^{-1}\)), 9 (625 cm\(^{-1}\)), 8 (651 cm\(^{-1}\)) and 12 cm\(^{-1}\) (1198 cm\(^{-1}\)), respectively, on the other hand that of other peaks is approximately 2 cm\(^{-1}\). This result supports our peak assignment.

4. Conclusions
We tried to detect the Raman peaks related to the proton tunneling in on 0-dimentional hydrogen bond system crystalline BHP and its deuterated material BDP at 40 K. It was observed that in BHP four additional peaks appear besides ordinary intra-molecule modes detected also in its deuterated material BDP. Considering a fact that their molecular structures are quite same except for the hydrogen bond part, it is possible that these Raman peaks are due to the frame vibration coupled with the proton motion. Further studies must be done.

References
[1] Blinc R 1960 *J. Phys. Chem. Solids* **13** 204
[2] Mochida T, Izuoka A, Sugawara T, Moritomo Y and Tokura Y 1994 *J. Chem. Phys.* **101** 7971
[3] Moritomo Y, Tokura Y, Mochida T, Izuoka A and Sugawara T 1995 *J. Phys. Soc. Jpn* **64** 1892
[4] Matsuo T, Kohno K, Inaba A, Mochida T, Izuoka A and Sugawara T 1998 *J. Chem. Phys.* **108** 9809
[5] Matsuo T, Kohno K, Ohama M, Mochida T, Izuoka A and Sugawara T 1999 *Europhys. Lett.* **47** 36