

# Dielectric Response in Bisquaric Acid Crystal: Possible Generation of Protonic Soliton in a Quasi-One-Dimensional Hydrogen-Bonded System

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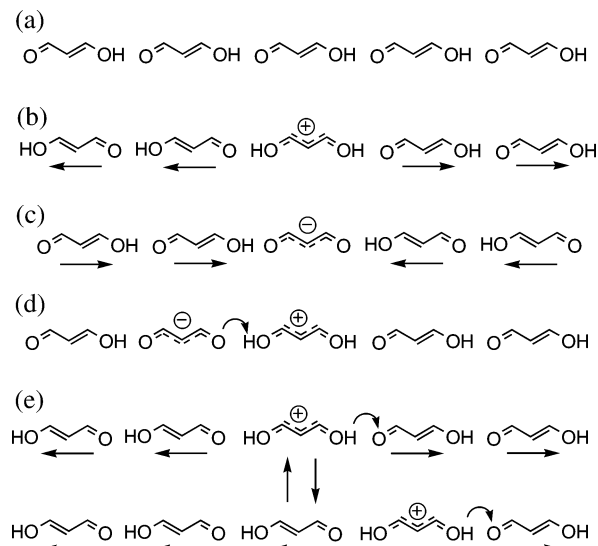
We investigated the proton dynamics of crystalline bisquaric acid ( $H_2BSQ$ ) in terms of the temperature and frequency dependence of its permittivity. It was found that the dielectric response of the  $H_2BSQ$  crystal exhibited two-step changes. With raising temperature, the dielectric permittivity increased slightly at 40 K. Whereas the temperature dependence of the permittivity at this temperature showed a large isotope effect, there was no frequency dependence of the permittivity. However, the permittivity increased largely at 290 K and showed distinct frequency dependence, although there was no-isotope effect on its characteristic temperature dependence. It was concluded that such a dielectric response of the  $H_2BSQ$  crystal was derived from the migration of protonic soliton coupled with the polarity inversion along the quasi-one-dimensional hydrogen-bonded chain.

## 1. Introduction

Proton transfer along hydrogen bonds plays an essential role not only in physical properties but also in biological functions.<sup>1–6</sup> The unique proton dynamics along a one-dimensional (1D) hydrogen-bonded chain has attracted a great deal of theoretical attention from the viewpoint of the solitonic proton transfer (protonic soliton).<sup>7–11</sup> The protonic soliton is a kind of a “kink soliton,” which is generated as a structural defect in a 1D system by thermal excitation and can freely migrate like a particle in the system. Although the soliton model has been theoretically proposed to describe dynamic properties in the 1D hydrogen-bonded system, dynamics of the protonic soliton have scarcely been studied experimentally because of the difficulty in constructing a 1D dynamic hydrogen-bonded chain that satisfies the theoretical model.

Although the high conductivity of ice is rationalized by the migration of ionic defects and Bjerrum (rotational) defects in hydrogen bonds,<sup>5</sup> the hydrogen-bonded network of ice is 3D. Accordingly, its dynamic behavior cannot be interpreted in terms of a 1D solitonic mechanism. However, 3-hydroxyenones are known to form 1D hydrogen-bonded systems by resonance-assisted hydrogen bonding.<sup>12,13</sup> One-dimensional hydrogen-bonded chains of *s-trans*-3-hydroxyenone are represented in Figure 1.<sup>14,15</sup> In the case of the 1D hydrogen-bonded chains, the charged kinks (protonated or deprotonated 3-hydroxyenones) exist at domain walls that separate the two oppositely arranged chains of molecular dipoles (Figure 1b and c).

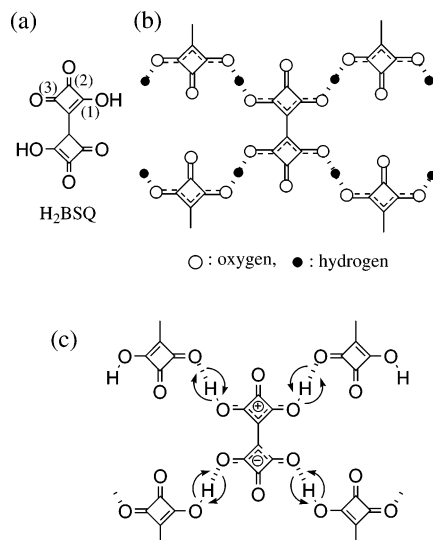
A pair of positive and negative kinks are created by shifting protons between adjacent molecules (Figure 1d). The concentration of kinks is determined by the thermodynamic equilibrium between the thermally generated kinks and the neutral species. The activation energy of kink generation may be approximated



**Figure 1.** (a–e) Schematic schemes of hydrogen-bonded *s-trans*-3-hydroxyenone chains. Molecular dipole moments are indicated by arrows. (a) Ordered structure of 1D hydrogen-bonded chain. (b and c) Positively or negatively charged ionic kink in the 1D hydrogen-bonded chain. The kink exists at the domain boundary, located between the oppositely polarized domains of the hydrogen-bonded chain. (d) Generation of a pair of kinks in the hydrogen-bonded chain. (e) Schemes to illustrate the migration of ionic kinks in the 1D hydrogen-bonded chain.

by the height of the energy barrier in the double minimum potential along the hydrogen-bonded chain. Because the kink site changes into a neutral site through proton transfer along the ionic hydrogen bond (Figure 1e), the charged kink migrates along the 1D hydrogen-bonded chain associated with the deformation of local molecular structure, if such a proton transfer occurs successively.

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**Figure 2.** (a) Molecular structure of H<sub>2</sub>BSQ. (b) Dynamically disordered quasi-1D hydrogen-bonded chains in the H<sub>2</sub>BSQ crystal. (c) Scheme of the zwitterionic structure in the H<sub>2</sub>BSQ crystal, and a pinning effect on the proton migration caused by the zwitterionic species in the H<sub>2</sub>BSQ crystal.

Accordingly, these charged kinks can be regarded as protonic solitons.<sup>1,7,8,14,15</sup> The closest example of the protonic soliton is the charged kink soliton in a doped polyacetylene.<sup>16</sup> In some crystals of 1D hydrogen-bonded 3-hydroxyenones, the existence of such charged kinks is supported by spectroscopic measurements.<sup>14</sup> However, no dynamic behavior of charged kinks has been investigated in the crystals of the 3-hydroxyenones.<sup>17–22</sup>

We have been intrigued by the hydrogen-bonding system in crystalline bisquaric acid<sup>23</sup> (H<sub>2</sub>BSQ in Figure 2), which is an extremely acidic oxoacid ( $\text{pK}_{\text{a}2} = -4.49$ ) containing two 3-hydroxyenone skeletons. In the H<sub>2</sub>BSQ crystal, the cross-conjugating  $\pi$  system of H<sub>2</sub>BSQ interconnects hydrogen-bonded chains that are formed by two squaryl moieties of H<sub>2</sub>BSQ molecules ( $\text{O}\cdots\text{O}$  distance = 2.523 Å), constructing a layered structure (Figure 2).<sup>23</sup> The H<sub>2</sub>BSQ crystal, therefore, can be regarded as a quasi-1D hydrogen-bonded system. Because H<sub>2</sub>BSQs are connected by strong hydrogen bonds with each other at four sites, the contribution of Bjerrum (rotational) kinks should be negligible, if any. Consequently, the hydrogen-bonded crystal of H<sub>2</sub>BSQ is an ideal system to apply the ADZ model,<sup>7,8,24</sup> which deals only with charged kinks. Moreover, X-ray analysis at room temperature revealed that the H<sub>2</sub>BSQ crystal has a symmetrical molecular structure with no  $\pi$ -bond alternation (space group  $P4_2/mnm$ ), indicating that the protons in the hydrogen bonds are statically or dynamically disordered.<sup>23</sup>

The solid-state NMR measurement also suggests the possibility of the proton migration in the crystal.<sup>25</sup> Thus, we examine here a possibility of proton dynamics of H<sub>2</sub>BSQ in terms of dielectric measurements and discuss the mechanism on the basis of a protonic soliton model.

## 2. Experimental Section

H<sub>2</sub>BSQ was synthesized according to the procedure of Liebeskind et al.<sup>23</sup> Single crystals of H<sub>2</sub>BSQ were obtained by slow evaporation from aqueous solution at ca. 70 °C; the largest crystal was ca. 0.5 × 0.8 × 0.8 mm<sup>3</sup>. D<sub>2</sub>BSQ crystals were obtained by crystallization from D<sub>2</sub>O (99.8%). Complete deuteration was confirmed by the disappearance of the OH stretching vibration in the IR spectrum. Dielectric measurements were performed with an LCR meter (Hewlett-Packard 4284A)

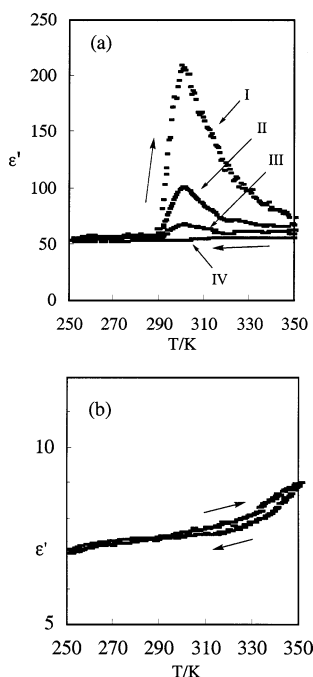
with alternating electric fields of 1–10 V/cm in a frequency range of 20–100 kHz. The crystals were sliced perpendicular to the direction of the measurements, and silver paste was painted on the sections as electrodes. The temperature of the sample was measured with an Au/Fe chromel thermocouple. The rate of decreasing or increasing temperature was 2 K/m, and the highest temperature measured was 400 K.

X-ray data collection was performed on a Rigaku AFC-7R four-circle diffractometer, with graphite monochromated MoK radiation ( $\lambda = 0.71073$  Å) at  $T = 103$  and 300 K.<sup>26</sup> Solid-state NMR spectra of crystals of H<sub>2</sub>BSQ were carried out on a Chemagnetics CMX300-NMR system operating at 75.6 MHz for <sup>13</sup>C in the CP/MAS mode. A powdered sample was packed in a zirconia rotor and spun at 4.7 kHz. The spectral conditions were as follows: spectral width was 40 kHz, proton 90° pulse was 5  $\mu$ s, cross polarization time was 5–20 ms, recycle decay was 10 s, and number of acquisitions was 1000. Chemical shifts were externally referenced to methyl carbons of hexamethylbenzene as a standard ( $\delta = 17.35$ ). The IR spectrum was recorded on a JASCO FT/IR-420 spectrometer. A KBr disk containing microcrystals of H<sub>2</sub>BSQ was attached to a CsI plate. For the low-temperature IR measurement, a Cryo-Mini Refrigeration System (Iwatani Cryo-Techno) was used. Thermal analysis was performed using a TA Instruments DSC differential scanning calorimeter (DSC2920 Modulated DSC) in the temperature range of 100–400 K with the same heating and cooling rates at 2 K/min.

## 3. Results and Discussion

**3.1. Dielectric Permittivity Derived from the Bisquaric Acid Crystal.** Measurement of the anisotropy of the dielectric permittivity of the crystal requires a single crystal of a sufficient size. Although tiny crystals (ca. 0.2 × 0.2 × 0.1 mm<sup>3</sup>) were obtained according to the reported method,<sup>22</sup> we prepared a single crystal with a reasonable size (ca. 0.8 × 0.8 × 0.5 mm<sup>3</sup>) by the recrystallization from an aqueous solution at ca. 70 °C.

The ac dielectric permittivity of a molecular crystal originates from the inversion of the polarization (in general, orientation polarization) of the constituent molecules against the applying ac electric field. The permittivity of weakly coupled antiferroelectrics increases at higher temperatures when the polarity inversion is thermally activated; however it decreases after having the maximum value, obeying Curie's law. This is because the contribution of the polarity inversion that follows the applying ac frequency decreases, owing to the enhancement of the thermal fluctuation. In fact, when the permittivity of the H<sub>2</sub>BSQ crystal was measured along the direction parallel to the molecular planes, the ac permittivity remained constant ( $\epsilon' \sim 50$ ) at temperatures lower than 290 K, but it showed an abrupt increase at ca. 290 K, having a maximum of  $\epsilon' \approx 180$  (800 Hz) at 300 K (Figure 3a). The dielectric response above 300 K exhibited a significant frequency dependence in the range of 800–100 kHz (Figure 3a, plots I, II, and III). Incidentally, the abrupt increase in the permittivity is not related to the structural phase transition because no changes in the space group of the crystal were detected by an X-ray diffraction experiment,<sup>26</sup> and no anomalies in endothermicity were observed by thermal analysis. The dependence of the permittivity on the ac frequency reflects the matching between the rate of polarity inversion of the sample and the ac frequency of the applying electric field. If the rate of the polarity inversion is extremely fast, such as in the case where proton migration occurs through a tunneling mechanism, then the permittivity does not exhibit frequency dependence.<sup>27</sup>

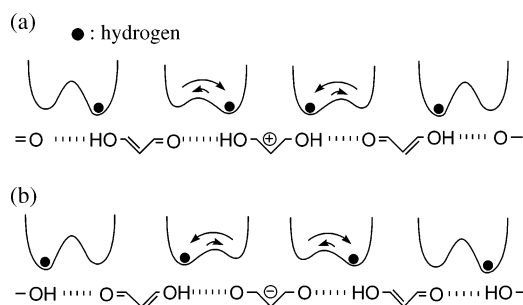


**Figure 3.** (a) Temperature and frequency dependence of ac permittivity  $\epsilon'$  of a  $\text{H}_2\text{BSQ}$  single crystal measured along the direction parallel to the 2D molecular plane: I, 800 Hz; II, 10 kHz; III, 100 kHz (I–III were measured in the increasing-temperature process), and IV was measured in a decreasing-temperature process (800 Hz, 10 kHz, and 100 kHz). (b) Temperature dependence of ac (800 Hz) permittivity  $\epsilon'$  of a  $\text{H}_2\text{BSQ}$  single crystal measured along the direction normal to the 2D molecular plane.

The temperature dependence of the permittivity measured along the direction parallel to the molecular planes exhibited a distinct thermal hysteresis. In the decreasing temperature process, the permittivity remained constant and showed no frequency dependence (Figure 3a, plot IV); however, when a supercooled sample was allowed to stand for several hours at 300 K, the permittivity nearly recovered to the original value. The detailed mechanism of this phenomenon will be discussed in section 3.5.

In contrast, only a small permittivity ( $\epsilon' \approx 10$ ), with almost no frequency dependence, was observed normal to the molecular planes in the same temperature range (Figure 3b). The large anisotropy in the permittivity is also reported in the case of the squaric acid crystal,<sup>28–30</sup> and the result is consistent with the interpretation that the permittivity originates not from the orientation polarization but from the proton dynamics along the hydrogen bonds within the hydrogen-bonded plane.<sup>29</sup>

To investigate the origin of the dielectric response of  $\text{H}_2\text{BSQ}$  crystal, we examined the dielectric property of the deuterated sample ( $\text{D}_2\text{BSQ}$ ). The space group of the  $\text{D}_2\text{BSQ}$  crystal was confirmed to be identical to that of  $\text{H}_2\text{BSQ}$  at room temperature.<sup>26</sup> It exhibited almost the same dielectric behavior and showed no deuteration effect on the temperature at which the permittivity was raised, although the distinct isotope effect was observed in the decreased process of the permittivity at lower temperatures in section 3.3. These results are in sharp contrast with those obtained for the squaric acid crystal with a 2D hydrogen-bonded network. In the squaric acid crystal, the intrinsic dielectric response is coupled with the structural phase transition and a large isotope effect on the phase transition temperature is observed. The absence of the phase transition in the  $\text{H}_2\text{BSQ}$  crystal might originate from the 1D nature of the hydrogen-bonding scheme.



**Figure 4.** Schematic of the proton potential around the ionic kink in the 1D hydrogen-bonded chain. Proton migration in the ionic hydrogen bonds involving (a) a cationic or (b) an anionic kink.

### 3.2. Migration of Charged Kinks in the $\text{H}_2\text{BSQ}$ Crystal.

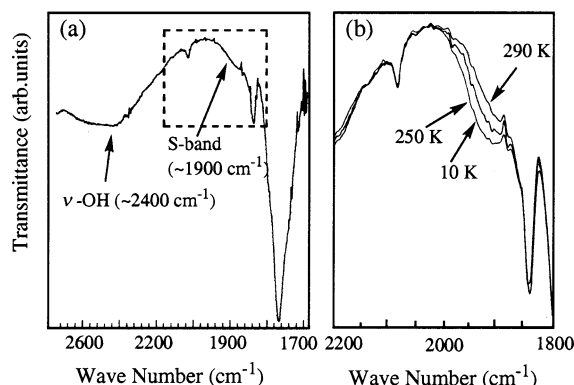
The remarkable dielectric response in the  $\text{H}_2\text{BSQ}$  crystal above 290 K turned out not to be derived from Debye's reorientation mechanism because the complex plane plots of  $\epsilon''$  against  $\epsilon'$  deviated widely from the Cole–Cole circular arc law and  $\epsilon''$  dispersed with decreasing frequencies. This tendency is characteristic of the case where the long-distance migration of charged species contributes to the permittivity.

As another possible mechanism of the high permittivity, the simultaneous proton-transfer model<sup>31</sup> was examined, taking the cooperativity of the system into account. The notion of the simultaneous proton transfer is used to describe the proton transfer in the closed (cyclic) hydrogen-bonded system, such as the carboxylic acid dimer<sup>32</sup> and calixarene,<sup>31</sup> where plural protons transfer simultaneously. The simultaneous proton transfer may also be possible in water, where limited hydrogen-bonded networks exist. A problem here, however, is that in a 1D hydrogen-bonded chain of the  $\text{H}_2\text{BSQ}$  crystal, the activation energy for a simultaneous transfer is predicted to be considerably high because the number of the hydrogen bonds is very large and there are dead ends on both sides of the 1D hydrogen-bonded chain.<sup>7</sup>

To understand the aforementioned dielectric properties associated with proton dynamics, we applied the notion of the dynamics of protonic solitons (charged kink solitons) generated in the  $\text{H}_2\text{BSQ}$  crystal. Around charged kinks, the height of the barrier to proton transfer along the ionic hydrogen bonds ( $\text{OH}^+ \cdots \text{O}$  or  $\text{OH} \cdots \text{O}^-$ )<sup>5,33</sup> is lower than that around the neutral species (Figure 4). In the ionic hydrogen bond, the proton donor is positively charged or the proton acceptor is negatively charged, hence the proton transfer is facilitated by the electrostatic interaction (Figure 1e).<sup>34</sup> The model, in which the migration of protonic solitons and polarity inversion are coupled with the successive proton transfer, does not conflict with the relatively slow dielectric response observed in the frequency dependence of the permittivity.

Support for the existence of charged kinks was obtained by vibration spectroscopic measurements on the  $\text{H}_2\text{BSQ}$  crystal (Figure 5). In some 1D hydrogen-bonded 3-hydroxyenones, the absorption called the S band is detected at ca.  $1800\text{ cm}^{-1}$ , which is assigned to the O–H stretching vibration around charged kinks.<sup>14</sup> The characteristic of the absorption band is that the band shape sharpened when a sample was cooled. In the crystal of  $\text{H}_2\text{BSQ}$ , we found the absorption at  $1900\text{ cm}^{-1}$ , and the intensity of the band showed a temperature dependence in the temperature range of 10–290 K. Because the temperature dependence was similar to that of 3-hydroxyenones, the absorption was assigned to the S band. Incidentally, the S band has not been detected in squaric acid crystals,<sup>35</sup> the dimensionality of which has a 2D character.





**Figure 5.** (a) S band in the infrared spectrum of the  $\text{H}_2\text{BSQ}$  crystal in a KBr pellet. The conventional OH stretching band was observed at  $2400\text{ cm}^{-1}$ . (b) Temperature dependence of the S band.

**3.3. Permittivity of  $\text{H}_2\text{BSQ}$  and  $\text{D}_2\text{BSQ}$  in the Low-Permittivity Region.** The disordered structure determined from the X-ray analysis and the detection of the S band in the IR spectrum support the existence of charged kinks in the low-permittivity region ( $T < 290\text{ K}$ ). Additional support for the protonic soliton model comes from finding that both  $\text{H}_2\text{BSQ}$  and  $\text{D}_2\text{BSQ}$  exhibited a slight decrease in  $\epsilon'$  at 40 and 125 K, respectively, in the low-permittivity region (Figure 5a and b). This small change in the permittivity was independent of the applied frequency (800–10k Hz). The decrease in the permittivity at lower temperatures, accompanying a large isotope effect, can be interpreted as the localization of protons or deuterons along the hydrogen-bonded chain. The hydrogen-bond distance of a  $\text{D}_2\text{BSQ}$  crystal is longer than that in a  $\text{H}_2\text{BSQ}$  crystal, whereas the interlayer distance of the  $\text{D}_2\text{BSQ}$  crystal is shorter than that of the  $\text{H}_2\text{BSQ}$  crystal.<sup>36</sup> The isotope effect upon the crystal structure is consistent with the higher localization temperature (125 K) in  $\text{D}_2\text{BSQ}$ .

On the basis of the mechanism of protonic soliton discussed in section 3.1, these results can be rationalized as follows. Over 290 K, the free kink migration coupled with successive proton transfer occurs and it shows high permittivity. Under 290 K, the free kink migration is frozen; however, strong ionic hydrogen bonds with low potential barriers, discussed in section 3.2, still exist around the frozen kink under 290 K (Figure 4). Therefore, the protons (deuterons) adjacent to the kinks can migrate even in the low-permittivity region (in  $\text{H}_2\text{BSQ}$ , 40K–290 K). We note that the proton migration occurs locally around the kink sites, not accompanying the successive proton transfer. Hence, the polarity inversion of the crystal is caused only by short-range proton migration, and the permittivity shows small but rapid dielectric response. Eventually, the local migration of protons and deuterons is completely frozen at 40 K in the  $\text{H}_2\text{BSQ}$  and at 125 K in the  $\text{D}_2\text{BSQ}$  crystal, respectively, and the permittivities of these crystals decrease further. Such proton dynamics are not found in squaric acid crystals or KDP ( $\text{KH}_2\text{PO}_4$ )-type dielectrics,<sup>37</sup> and it can be regarded as a characteristic of this system. A problem of the above mechanism is how the kinks are frozen at 290 K in the  $\text{H}_2\text{BSQ}$  crystal. A plausible mechanism will be discussed in section 3.5.

**3.4. Solid States  $^{13}\text{C}$  NMR Spectra.** The temperature dependence of the  $^{13}\text{C}$  NMR CP/MAS spectrum of the  $\text{H}_2\text{BSQ}$  crystals was reported recently.<sup>25</sup> The spectrum consists of three lines at 202, 190, and 158 ppm, and the peak at 202 ppm was assigned to C(1) and C(3) carbon atoms (Figure 1). We reproduced the spectrum and confirmed that the assignments are reasonable because the intensity of the peak at 202 ppm changed significantly when the contact time was varied. The

decrease in the bandwidth of this signal at elevated temperatures was ascribed to the possible exchange between these carbon atoms due to the intermolecular proton transfer.<sup>25</sup> This interpretation is strongly supported by the current dielectric measurement, indicating that rapid proton transfer occurs at temperatures higher than ca. 290 K. Incidentally, signals of the charged kinks are not observed because the concentration of those kinks is much lower than the detection limit.

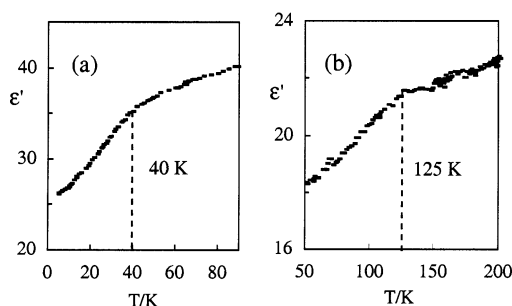
**3.5. Trapping and Release of Mobile Charged Kinks.** The X-ray crystallographic analysis on the  $\text{H}_2\text{BSQ}$  crystal at 300 K revealed that the molecular skeleton of  $\text{H}_2\text{BSQ}$  was symmetrical, the bond alternation being diminished. The disordered structure in the crystal was interpreted in terms of the dynamic disorder on the basis of the dielectric measurement. The low-temperature X-ray analysis at 100 K revealed that the molecular structure was also symmetrical even at lower temperatures. This is caused by the static disorder derived from the suppression of free migration of charged kinks in the hydrogen-bonded chain. We note that the structural transition of the  $\text{H}_2\text{BSQ}$  crystal does not occur, although it occurs in the case of the squaric acid crystal.

Accordingly, the sudden rise in the dielectric response at temperatures higher than 290 K was not derived from the generation of kinks<sup>38</sup> but from the release of the trapped kinks already present in the hydrogen-bonded chain. However, the absence of dielectric response of the  $\text{H}_2\text{BSQ}$  crystal in the temperature-descending process (Figure 3a, plot IV) can be explained by applying the notion of the trapping effect of the kinks. The thermal energy for the kinks to move freely along the hydrogen-bonded chain becomes deficient in the temperature-descending process, and the kinks are trapped in some binding sites. Because this state is a nonthermally equilibrated state and the location of protons is disordered, it can be regarded as a glassy state (section 3.1).

Proton conduction in the hydrogen-bonded system of ice has been discussed by assuming that the number of charged defects is fixed. They are trapped by some defects at lower temperature, but they are released at elevated temperatures.<sup>39</sup> However, the mechanism of the trapping of kinks has not been discussed in detail. In the case of the  $\text{H}_2\text{BSQ}$  crystal, a possible trapping mechanism could be discussed on the basis of the molecular structure of  $\text{H}_2\text{BSQ}$ .

Because the neighboring hydrogen-bonded chains are correlated by the  $\pi$ -conjugating system of the  $\text{H}_2\text{BSQ}$  skeleton with each other, the interchain interaction cannot be ignored. Therefore, the  $\text{H}_2\text{BSQ}$  crystal is regarded as an interacting 1D system in the lower temperature region ( $< 290\text{ K}$ ). In this respect, we need to consider the role of zwitterionic structures of  $\text{H}_2\text{BSQ}$  in fixing oppositely charged kinks (Figure 2c); namely, the independent migration of the oppositely charged kinks is suppressed by the Coulombic attraction within the zwitterionic structure when the temperature was decreased. This mechanism may be designated as a kind of an intramolecular pinning effect, which is characteristic of the molecular structure of  $\text{H}_2\text{BSQ}$ .

When a pair of oppositely charged kinks that are independently migrating on the neighboring 1D chain encounter each other on the same  $\text{H}_2\text{BSQ}$  molecule, the pair of charged kinks lose their mobility and are frozen as a zwitterion under 290 K. If a proton transfer occurs between the zwitterion and the adjacent neutral molecules, then the oppositely charged kinks must be separated. However, such a process would be energetically unfavorable. Therefore, the local proton migration from 40 to 290 K in the  $\text{H}_2\text{BSQ}$  crystal is explained by the restriction of the free migration of the charged kinks by the trapping effect



**Figure 6.** Isotope effect observed in the permittivity (800 Hz) in the low-permittivity region for (a) H<sub>2</sub>BSQ and (b) D<sub>2</sub>BSQ.

of the zwitterionic species. At elevated temperatures (>290 K), the charged kinks are released from the Coulombic attraction, and they can migrate freely along the 1D hydrogen-bonded chain. The absence of an isotope effect in the generation of the high permittivity can also be rationalized by this model; namely, the rate-determining step for the migration of charged kinks corresponds to the release of charged kinks from the interchain Coulombic interaction mediated by the zwitterionic structure (Figure 6).

#### 4. Conclusions

The dielectric response in the H<sub>2</sub>BSQ crystal was investigated precisely, and it was argued that the obtained dielectric response is derived from the solitonic behavior characteristic to the quasi-1D hydrogen-bonded system. Although the free migration of charged kinks is suppressed at lower temperatures than 290 K, the local motion of the protons around the ionic species still remains, and this local motion is completely quenched under 40 K for H<sub>2</sub>BSQ and 125 K for D<sub>2</sub>BSQ. This system provides a long-awaited model for the investigation of the protonic soliton.

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- (36) The lattice constant of D<sub>2</sub>BSQ was *a* = 8.004(1), *b* = 8.004(1), *c* = 5.288(2) Å, *V* = 338.81 Å<sup>3</sup>, *Z* = 8. The hydrogen-bond distance is 2.523-(1) Å for H<sub>2</sub>BSQ and 2.5525(2) Å for D<sub>2</sub>BSQ. The interlayer distance is 2.674(1) Å for H<sub>2</sub>BSQ and 2.644(1) Å for D<sub>2</sub>BSQ.
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- (38) There is a possibility that the charged kinks are generated in terms of the proton transfer between adjacent neutral species by the external electric field and that the dielectric response of the crystal is derived from the motion of these ionic pairs. However, as pointed out by the theoretical studies, the potential barrier to the proton transfer between neutral species is high and the proton transfer is not practically accelerated by the application of the normal electric field. In fact, the permittivity of H<sub>2</sub>BSQ crystal did not change when the electric field was changed in the range of 1–10 V/cm.
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