

Phonon-assisted proton(deuteron) transfers leading the antiferro-electric ordering in superprotonic conductors $\text{Cs}_3\text{H(D)}(\text{SeO}_4)_2$

Proton conduction is a key functionality to improve a high-performance fuel cell that is a fundamental technology to reduce CO_2 emissions and to achieve a hydrogen society. In general, proton conduction is phenomenologically discussed with activation-type motions as a diffusion process. In crystalline proton conductors, a proton–phonon (PP) interaction is significant to understand microscopic-transfer mechanisms because the proton never transfers individually but interacts with a lattice system. Nevertheless, little knowledge on PP interactions has been obtained so far in protonic systems. Among a variety of proton conductors, we have focused on $\text{Cs}_3\text{H(D)}(\text{SeO}_4)_2$ that exhibits superprotonic conduction above T_{SPC} and antiferroelectric (AF) ordering below T_{AF} (Fig. 1 (a)), because the good single crystal is obtained.

The crystal structure on the ab plane of localized phases III and IV is shown in Fig. 1(b), where the lattice constant is summarized in the table. Two SeO_4 tetrahedra are connected through a hydrogen bond between apical O(2) and O'(2) in the form of dimer (Fig. 1(c)). The proton and deuteron possess two equivalent sites in between O(2) and O'(2). A remarkable isotope effect relevant to the AF ordering was known about 40 years ago (Fig. 1(a)); $T_{\text{AF}} = 50$ K ($\text{Cs}_3\text{H}(\text{SeO}_4)_2$) and 168 K ($\text{Cs}_3\text{D}(\text{SeO}_4)_2$). Similar

isotope effects are observed in the corresponding systems such as $\text{Rb}_3\text{H(D)}(\text{SeO}_4)_2$, and ferroelectric materials like potassium dihydrogen phosphate (KDP). Employing a wide range of infrared spectroscopies combined with first principles calculations and $^1\text{H-NMR}$ experiments, we have clarified the difference of AF-ordering mechanisms and the role of PP interactions in $\text{Cs}_3\text{H}(\text{SeO}_4)_2$ and $\text{Cs}_3\text{D}(\text{SeO}_4)_2$ [1,2].

Absorbance spectra below 300 K were measured at $5\text{--}8000\text{ cm}^{-1}$ utilizing a terahertz time-domain spectrometer, and a FT-IR spectrometer equipped with a Cassegrain microscope. Especially in far-infrared range, the single-domain crystal with about 1 mm in diameter is quite difficult to measure with usual spectrometers. Thanks to the microscopic spectrometer facilitated at SPing-8 BL43IR providing strong far-infrared light, we have successfully detected the polarized absorbance spectra.

In the far-infrared spectra of $\text{Cs}_3\text{H}(\text{SeO}_4)_2$ (Fig. 2(a)) and $\text{Cs}_3\text{D}(\text{SeO}_4)_2$ (Fig. 2(b)), a libration and SeO_4 -tetrahedral deformations accompanied with a O-Se-O bending (def_{bend} mode) appear at 180 and $300\text{--}450\text{ cm}^{-1}$, respectively [1,2]. The libration in $\text{Cs}_3\text{H}(\text{SeO}_4)_2$ exhibits a spectral splitting at $30\text{--}70$ K, while such anomaly is never observed in $\text{Cs}_3\text{D}(\text{SeO}_4)_2$. In Fig. 2(c), the splitting for a polarization at T_{AF} in $\text{Cs}_3\text{H}(\text{SeO}_4)_2$ is reproduced with two Lorentzian curves. The vibrational motif of libration illustrated in Fig. 2(d) induces a characteristic modulation of O(2)-O'(2) distance. From the mid-infrared spectrum, anomalous OH stretching mode proves that the proton anharmonically couples to the libration, and thereby the PP interaction plays the important role to generate the AF ordering [1]. In $\text{Cs}_3\text{D}(\text{SeO}_4)_2$, anomalous enhancements of the integrated absorbance (Fig. 2(e)) are observed at around T_{AF} in the 310-cm^{-1} def_{bend} mode that is painted in blue in Fig. 2(b), and the vibrational motif is depicted in Fig. 2(f). Taking the anharmonicity of OD stretching mode into account, the deuteron is found to couple to the 310-cm^{-1} def_{bend} mode [2]. Therefore, the proton and deuteron interact to the different phonon modes.

The proton and deuteron have to transfer between the equivalent sites to achieve the AF arrangement. According to the $^1\text{H-NMR}$ measurements, conventional thermal hopping in a rigid double-minimum potential (Fig. 3(a)) diminishes below 150 K [1]. As the modulation of O(2)-O'(2) distance is huge enhanced through fluctuations towards the AF ordering in

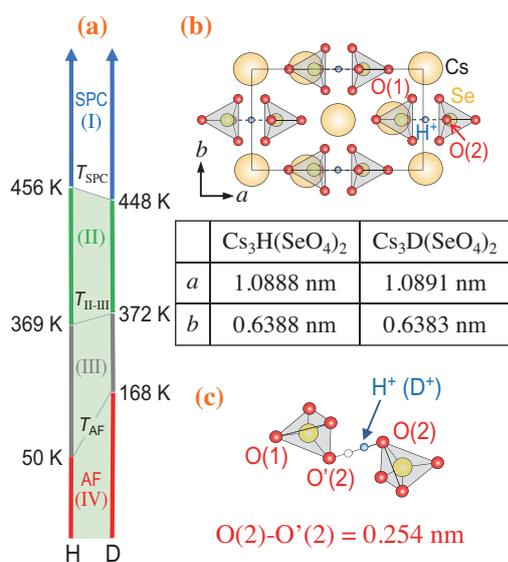


Fig. 1. (a) Transition temperatures in $\text{Cs}_3\text{H}(\text{SeO}_4)_2$ and $\text{Cs}_3\text{D}(\text{SeO}_4)_2$. (b) Crystal structure on the ab plane and lattice constants. (c) Two equivalent sites in O(2)-O'(2) of the dimer.

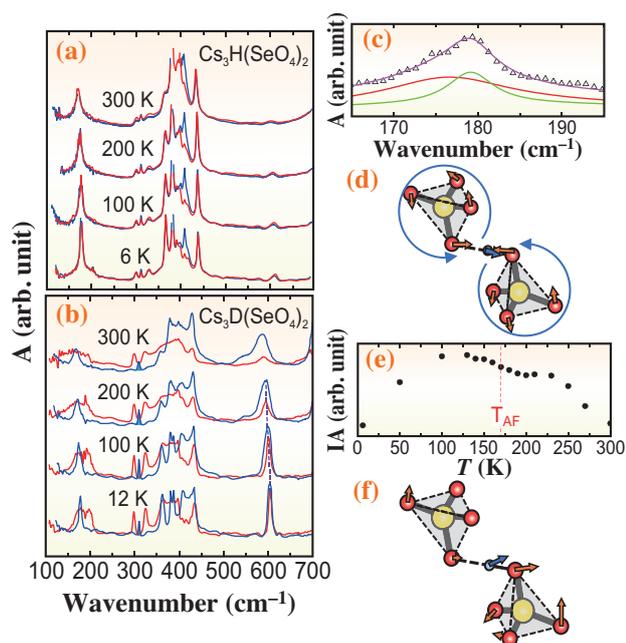


Fig. 2. (a, b) Absorbance (A) of $\text{Cs}_3\text{H}(\text{SeO}_4)_2$ and $\text{Cs}_3\text{D}(\text{SeO}_4)_2$ in far-infrared range. (c, d) Splitting and vibrational motif of the libration in $\text{Cs}_3\text{H}(\text{SeO}_4)_2$. (e, f) Integrated absorbance (IA) and vibrational motif of the 310-cm^{-1} def_{str} mode in $\text{Cs}_3\text{D}(\text{SeO}_4)_2$.

$\text{Cs}_3\text{H}(\text{SeO}_4)_2$, the wave functions of two equivalent sites can overlap, and simultaneously a dynamical proton tunneling yields the splitting of the ground state as shown by red lines in Fig. 3(b). Since each level strongly couples to the libration, the split bands emerge in the far-infrared time scale. This

phenomenon corresponds to a phonon-assisted proton tunneling (PAPT) associated with the libration, and hence quantum fluctuations conduct the AF ordering.

A splitting is never observed in the spectra of $\text{Cs}_3\text{D}(\text{SeO}_4)_2$, though the anomalous integrated absorbance of 310-cm^{-1} def_{bend} mode represents the increase of oscillator strength through huge modulations of the O(2)-O'(2) distance [2]. The modulation dynamically suppresses the potential-barrier height (Fig. 3 (c)), and then a phonon-assisted deuteron hopping (PADH) associated with the 310-cm^{-1} def_{bend} mode generates classical fluctuations to lead the AF ordering. The isotope effect is concluded to change the phonon that helps the transfer. Since the 310-cm^{-1} def_{bend} mode is energetically larger than the libration, $\text{Cs}_3\text{D}(\text{SeO}_4)_2$ possesses higher T_{AF} than $\text{Cs}_3\text{H}(\text{SeO}_4)_2$.

Finally, we would like to mention the 610-cm^{-1} band that exhibits the most remarkable isotope effect. The absorbance spectrum obtained by the first principles calculation has no bands at $500\sim 700\text{ cm}^{-1}$. The 610-cm^{-1} band is not attributed to phonons and molecular vibrations, but to a collective excitation relevant to a classical hopping, because the barrier height coincides with the result evaluated from the $^1\text{H-NMR}$ measurement [1]. The intensity in $\text{Cs}_3\text{D}(\text{SeO}_4)_2$ (Fig. 2(b)) is about ten times as large as one in $\text{Cs}_3\text{H}(\text{SeO}_4)_2$ (Fig. 2(a)) [2]. In $\text{Cs}_3\text{H}(\text{SeO}_4)_2$, the PAPT associated with the 440-cm^{-1} def_{bend} mode becomes dominant at $70\text{--}250\text{ K}$, so that very few protons contribute to the classical hopping. On the other hand, all the deuterons contribute to the classical hopping, and consequently the 610-cm^{-1} band in $\text{Cs}_3\text{D}(\text{SeO}_4)_2$ has large intensity compared to $\text{Cs}_3\text{H}(\text{SeO}_4)_2$.

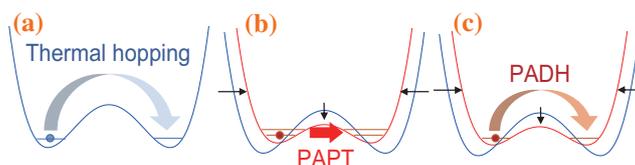


Fig. 3. Schematic illustrates of double minimum potential for thermal hopping (a), PAPT (b) and PADH (c).

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References

- [1] H. Matsui *et al.*: J. Chem. Phys. **152** (2020) 154502.
- [2] H. Matsui, K. Fukuda, S. Takano, Y. Ikemoto, T. Sasaki and Y. Matsuo: J. Chem. Phys. **156** (2022) 204504.