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# The Infrared Spectra and the Antiferroelectric Phase Transition of Copper Formate Tetrahydrate

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The infrared spectra of copper formate tetrahydrate are measured in the frequency region from 4000 to 24 cm$^{-1}$ at various temperatures. This compound is known to undergo an antiferroelectric phase transition at $-37.7$°C. The bands due to the librational and translational modes of the crystalline water molecules in the antiferroelectric phase are quite different from those in the paraelectric phase, while no appreciable differences between the spectra in the two phases are observed for other bands. Those facts agree with the results obtained by the crystallographic study, which show that the ordering of the orientation of the water molecules occurs at the phase transition. The similarity of the librational and the translational modes of the water molecules to those of ice is also discussed.

Solid copper formate tetrahydrate, $Cu(HCOO)_2\cdot 4H_2O$, undergoes an antiferroelectric phase transition at $-37.7$°C, and the transition temperature shifts to $-27.7$°C, when the crystalline water is deuterated.[1–3] The crystal structure of the paraelectric phase (above the transition temperature) was determined by means of X-ray diffraction by Kiriyama, Ibamoto, and Matsuo[4] and by means of neutron diffraction by Okada, Cromer, and Almodovar[5]; they found the space group of the crystal to be $P2_1/a$—$C_{2h}^5$, with two formula units per unit cell. The crystal consists of alternative layers, one of copper formate and one of crystalline water, parallel to the *ab* plane. The orientation of the crystalline water molecules is disordered; this disorder is similar to that observed in ice.[5] Okada *et al.* suggested that a two-dimensional ordering of the orientation of the water molecules occurs at the phase transition. Turberfield[6] studied the crystal structure of $Cu(HCOO)_2\cdot 4D_2O$ by means of neutron diffraction at temperatures ranging from 4.2 to 253°K and concluded that the ordering process at the transition temperature involves a cell doubling along the *c* axis. The ordered structure of the crystalline water molecules in the antiferroelectric phase was studied by means of deuteron magnetic resonance by Soda and Chiba.[7,3] They proposed that the ordered layer of the water molecules has a 2-fold screw axis symmetry. The corresponding space group is $P2_1/n$. The structures of the copper formate and of the disordered and ordered water molecules layers are shown in Figs. 1 and 2 respectively.

The infrared spectra of the compound were measured by Kuroda and Kubo.[9] They analyzed the bands due to the copper formate layer, assuming a planar model of the space group $P4/mbm$—$D_{4h}^5$. The librational modes of the crystalline water molecules were observed in the frequency region from 800 to 500 cm$^{-1}$ [9]. The translational modes of the water molecules, expected to

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[1] H. Kiriyama, This Bulletin **35**, 1199 (1962).

[2] K. Okada, *Phys. Rev. Lett.*, **15**, 252 (1965).

[3] K. Okada and H. Sugie, *J. Phys. Soc. Japan*, **25**, 1128 (1968).

[4] R. Kiriyama, H. Ibamoto, and K. Matsuo, *Acta Crystallogr.*, **7**, 482 (1954).

[5] K. Okada, M. I. Kay, D. T. Cromer, and I. Almodovar, *J. Chem. Phys.*, **44**, 1648 (1966).

[6] K. C. Turberfield, *Solid State Commun.*, **5**, 887 (1967).

[7] G. Soda and T. Chiba, *J. Chem. Phys.*, **48**, 4328 (1968).

[8] G. Soda and T. Chiba, *J. Phys. Soc. Japan*, **26**, 249 (1969).

[9] Y. Kuroda and M. Kubo, *Sepectrochim. Acta*, **23A**, 2779 (1967).

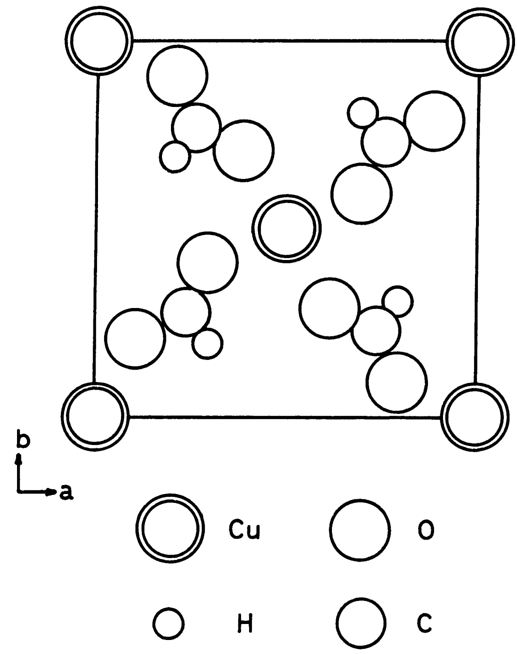

Fig. 1. Structure of the copper formate layer.[5]

appear in the frequency region lower than 350 cm$^{-1}$, were not yet measured. They assigned the CH stretching, the $CO_2$ asymmetric stretching, the $CO_2$ symmetric stretching, the CH in-plane and the CH out-of-plane bending, and the $CO_2$ scissoring vibrations to the bands at 2910, 1562, 1384, 1366, 1050, and 834 cm$^{-1}$ respectively. In the present work, the infrared spectra of the solid in the frequency region from 4000 to 24 cm$^{-1}$ are measured at various temperatures, as the librational and the translational modes of the water molecules are expected to give some information about the phase transition. The spectrum above 1000 cm$^{-1}$ is not discussed in the present paper, because our results do not differ from those obtained by Kuroda and Kubo.[9]

## Experimental

The sample was prepared by the method reported by Okada *et al.*[5] Single crystals grown from an aqueous solution were crushed to prepare Nujol mull for the infrared absorption measurements. The crystalline water was deuterated by keeping the powdered sample in a desiccator with heavy water for a few weeks. As the compound reacts with potassium bromide, plates of Ge, KRS-5, and polyethylene were used for the measurement of the spectra. The infrared spectra were usually recorded on JASCO model 402-G (from 4000 to 400 cm$^{-1}$), Hitachi model EPI-L (from 700 to 200 cm$^{-1}$), and Hitachi model FIS-1 (from 500 to 60 cm$^{-1}$) grating spectrophotometers. A Hitachi model FIS-21 single-beam grating spectrophotometer of the Cryogenic Center, University of Tokyo, was also used for the measurement in the frequency region from 180 to 24 cm$^{-1}$. The temperature was measured with a copper constantan thermocouple, which was inserted into the plates through a small hole. The temperatures shown in the figures were measured within an accuracy of $\pm 2$°K for the measurement of the frequency region of the librational modes and within an accuracy of $\pm 1$°K for the measurement of the frequency region of the translational modes.

## Results and Discussion

*(1) Temperature Dependency of the Spectra.* The infrared spectra in the frequency region from 1000 to

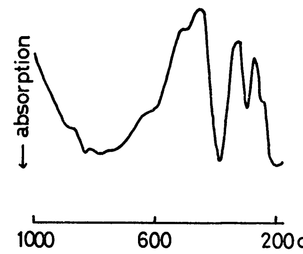

Fig. 3. Infrared spectra in the frequency region from 1000 to 180 cm$^{-1}$ of $Cu(HCOO)_2 \cdot 4H_2O$ at room temperature.

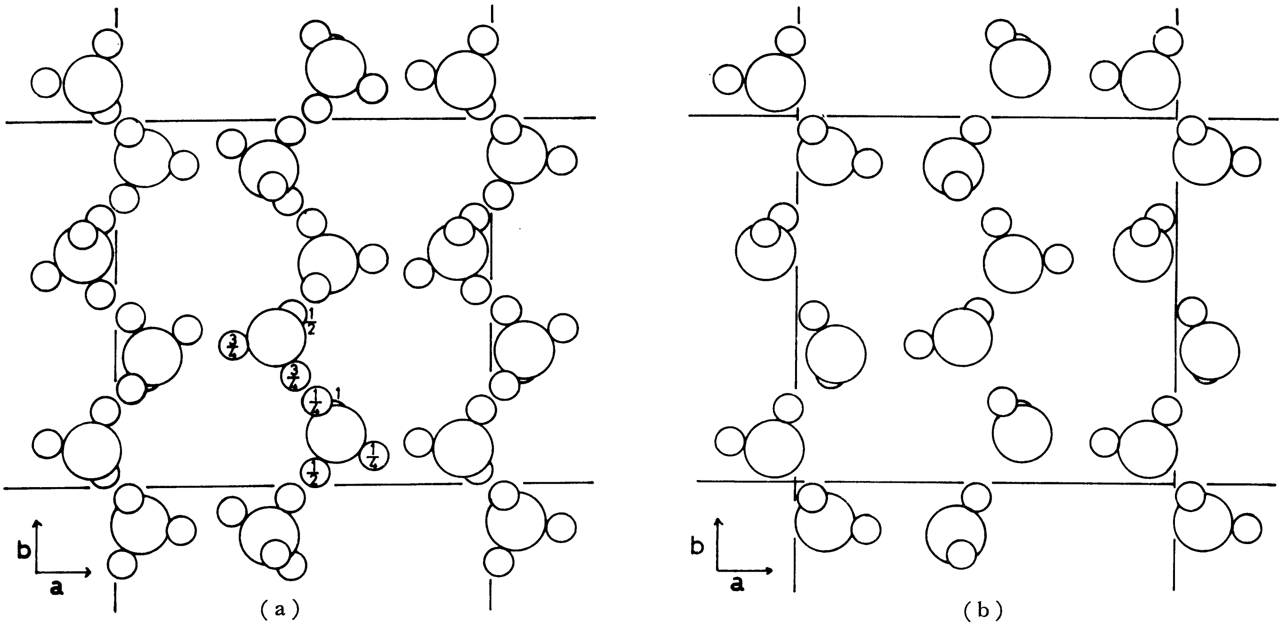

Fig. 2. Structure of the $H_2O$ layers (a) in the paraelectric phase[5] and (b) in the antiferroelectric phases.[8] The large and the small circles represent the oxygen and the hydrogen atoms of water molecules, respectively. The number on small circles indicates the statistical weight of each hydrogen atom.

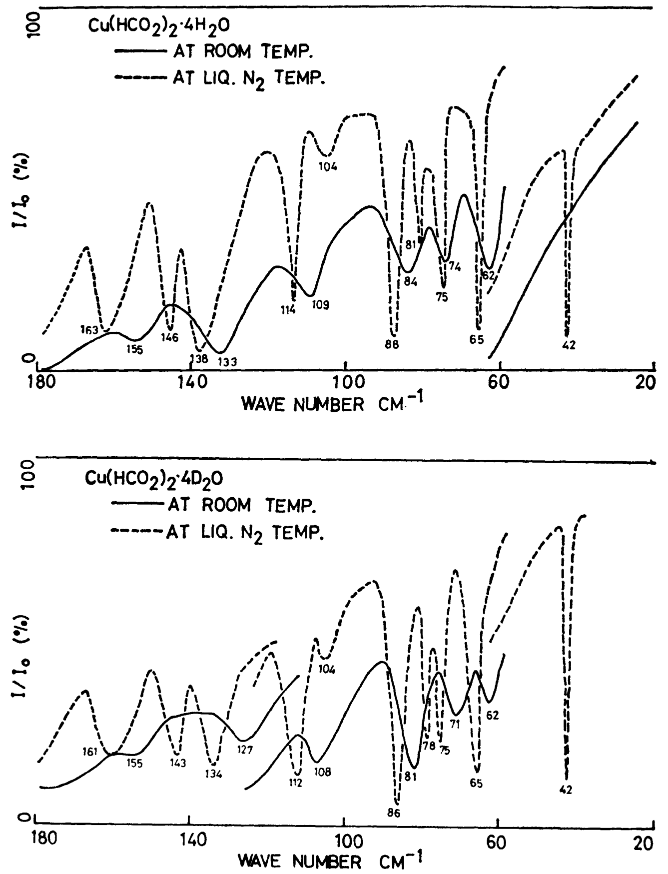

Fig. 4. Far infrared spectra in the frequency region from 180 to 24 $cm^{-1}$ of $Cu(HCOO)_2 \cdot 4H_2O$ and $Cu(HCOO)_2 \cdot 4D_2O$ (70—80% of the crystalline water is deuterated) at room and liquid nitrogen temperatures.

180 $cm^{-1}$ of $Cu(HCOO)_2 \cdot 4H_2O$ are shown in Fig. 3. The spectra below 180 $cm^{-1}$ at room temperature and the temperature of liquid nitrogen for $Cu(HCOO)_2 \cdot 4H_2O$ and $Cu(HCOO)_2 \cdot 4D_2O$ are also shown in Fig. 4. The spectra at low temperatures in the frequency region from 700 to 450 $cm^{-1}$ and below 180 $cm^{-1}$ are quite different from those at room temperature. Spectral change in the librational and the translational modes of crystalline water upon temperature depression has been observed for several salts, such as $CuCl_2 \cdot 2H_2O$[10] and $Li_2SO_4 \cdot H_2O$,[11] although no phase-transition phenomenon has been reported for these compounds. In order to confirm that the spectral change observed in copper formate tetrahydrate arises from the antiferroelectric phase transition, the spectra were recorded at various temperatures in the frequency region from 700 to 450 $cm^{-1}$ and from 90 to 60 $cm^{-1}$. The results, shown in Figs. 5 and 6, indicate that the spectral change occurs at the transition temperature. The discontinuity in the spectra with the temperature depression found in the bands due to the translational and the librational modes of the crystalline water molecules (see the later discussion of the assignment) is not found in the bands due to the formate group and the $H_2O$ stretching and the bending vibrations. These

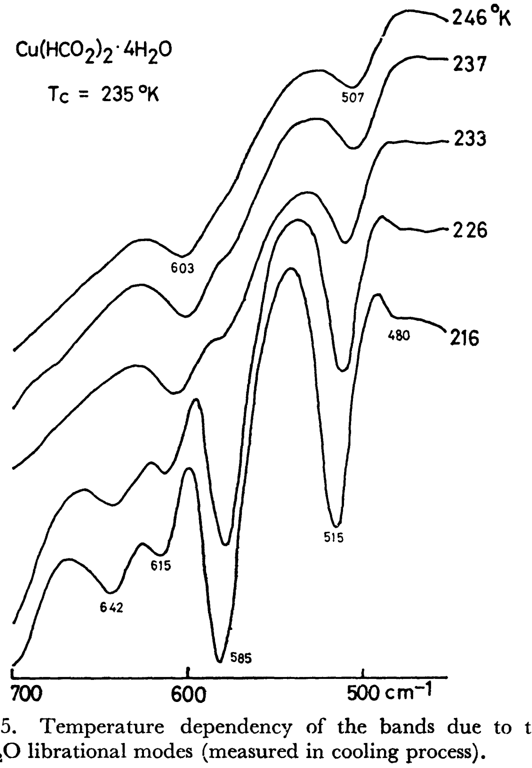

Fig. 5. Temperature dependency of the bands due to the $H_2O$ librational modes (measured in cooling process).

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[10] K. Fukushima, This Bulletin, **44**, 372 (1971).

[11] S. Meshizuka and H. Takahashi, Preceedings of the 24th Annual Meeting of Chemical Society of Japan, **1**, 229 (1971).

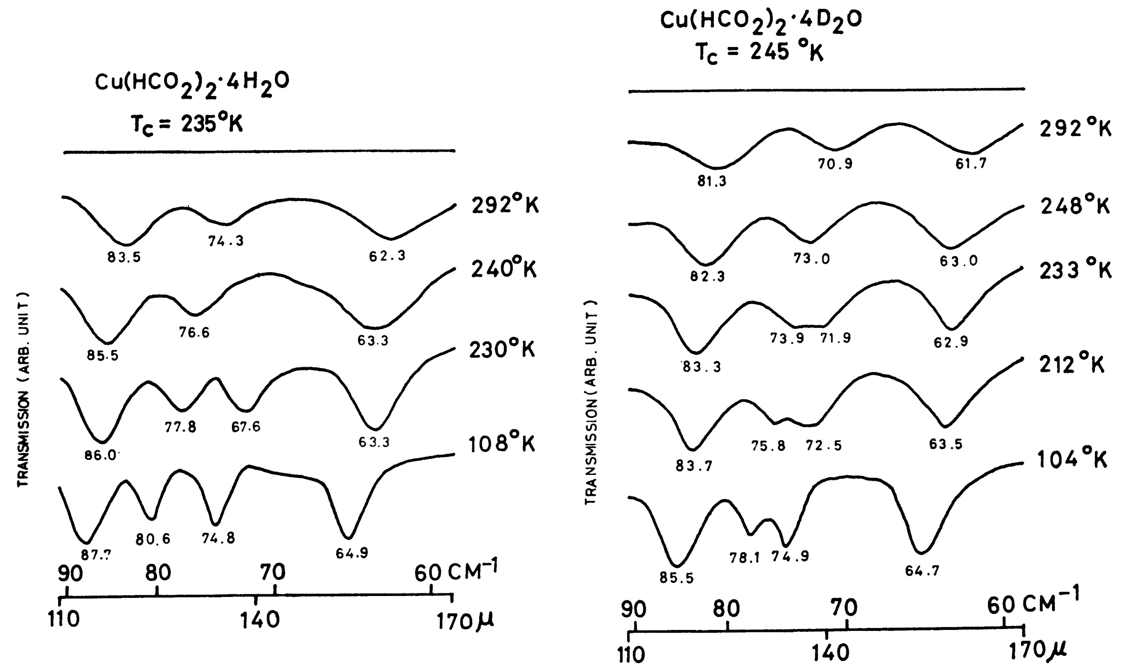

Fig. 6. Temperature dependency of the bands in the frequency region of the $H_2O$ and $D_2O$ translational modes.

facts agree with the finding obtained by other methods—that the crystalline water molecules are connected with the antiferroelectric phase transition.

*(2) The Librational Modes of the Crystalline Water Molecules.* The broad band covering the frequency region from 900 to 450 cm$^{-1}$ in Fig. 3 was assigned to the $H_2O$ librational modes by Kuroda and Kubo.[9] This assignment was confirmed by the deuteration of the crystalline water, on which the broad band shifted to the lower frequency region around 550 cm$^{-1}$ and left the $CO_2$ scissoring vibration band at 834 cm$^{-1}$. The disordered structure of the crystalline water in the paraelectric phase, shown in Fig. 2a, is somewhat similar to that found in ice.[5] The infrared and Raman spectra of ice were measured by Whalley *et al.*[12] The librational bands of ice I, which has an disordered structure, form a broad band covering the frequency region from 1000 to 400 cm$^{-1}$, while those of ice II and III give a good deal of a fine structure below 700 cm$^{-1}$. They explained that this fine structure arose from the ordering of the hydrogen atoms in ice II and III because of the disappearance of the fine structure in partially-deuterated ice II or III. The librational band of ice I is similar to that of the crystalline water of the formate in the paraelectric phase; those of ice II and III are also similar to that of the formate in the antiferroelectric phase. The spectra of the librational modes of the partially-deuterated crystalline water molecules of the formate below the transition temperature do not give such a fine structure as is observed for the ordinary water molecules of the formate. These facts indicate that the transition from the paraelectric to the antiferroelectric phase involves the ordering of the orientation of the crystalline water molecules, as was pointed out by a crystallographic study.[5]

*(3) The Spectra below 400 cm$^{-1}$.* The vibrations which are expected to appear below 400 cm$^{-1}$ can be classified into three groups. The first group, A, includes the vibrations due to the copper formate layer, except for the intramolecular vibrations of the $HCO_2$ group and three acoustic modes of the layer. In the paraelectric phase, these vibrations are classified as $6a_g+8a_u+6b_g+7b_u$; that is, fifteen vibrations are infrared active. The second group, B, includes the translational modes of the crystalline water molecules, except for three acoustic modes of each layer. There are 42 modes $(11a_g+10b_g+11a_u+10b_u)$ in the antiferroelectric phase. The rest of the vibrations (Group C) are due to the acoustic modes of each layer. There are three modes for the paraelectric phase $(a_u+2b_u)$ and nine for the antiferroelectric phase $(a_g+3a_u+2b_g+3b_u)$, except for three acoustic modes of the crystal.

The number of the bands observed below 400 cm$^{-1}$ is much less than expected. It is not the purpose of the present paper to assign all the observed bands. We may say, at least, that most of the bands below 180 cm$^{-1}$ can be assigned to the vibrations of group B, because the translational vibrations of water molecules in ice are located in this frequency region,[12] and that most of the bands below 180 cm$^{-1}$ of the formate shift more or less to the lower frequency region on the deuteration of the crystalline water molecules, as is shown in Fig. 4. The following discussion may explain the difference between the spectra below 180 cm$^{-1}$ in the para- and the antiferroelectric phases. Whalley and Bertie discussed the vibrational spectra of orientationally-disordered crystals.[12a] Their conclusion was that all the translational lattice vibrations of the orientationally-disordered crystal can be active in both the Raman and infrared spectra. They analyzed the translational vibrations of ice I,[12b] considering that the features in the

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[12] a) J. E. Bertie and E. Whalley, *J. Chem. Phys.*, **40**, 1637, 1646 (1964). b) *ibid.*, **46**, 1271, 1264 (1967). c) M. J. Taylor and E. Whalley, *ibid.*, **40**, 1660 (1964). d) J. E. Bertie, H. J. Labbe, and E. Whalley, *ibid.*, **49**, 775 (1968).

infrared spectrum correspond to similar features in the density of states of the lattice vibrations. The far infrared spectra of ice I show a very broad band with a sharp maximum at 229.2 cm$^{-1}$ and several shoulder bands, while the spectra of ice II show sharp maxima at 237.1, 186.4, 151.4, 136.1, and 106.5 cm$^{-1}$, plus a few shoulder bands.[12d] Makita and Seo measured the dielectric constant of the formate and reported the relaxation time to be $10^{-6}$—$10^{-7}$ sec,[13] which is much larger than the period of the translational lattice vibrations of the crystalline water molecules ($10^{-11}$—$10^{-12}$ sec). That is, the orientation of the water molecules of the formate is disordered during the period of the translational lattice vibrations of the water molecules. Accordingly, all of the translational lattice vibrations, not only with the wave vector $k\sim 0$, but also with $k\neq 0$, are infrared active in the paraelectric phase. In the antiferroelectric phase, the structure is ordered and the ordinary selection rule of the symmetry $C_{2h}$ holds for the infrared absorption.

Figure 7 shows the vibrational modes of Group C. The interatomic distances of Cu–O$_W$ (2.38 Å) and H$_W$–O$_F$ (1.88 Å) are about the same as the distances of Cu–O$_F$ (2.00 Å) and the H$_W$–O$_W$ hydrogen bond (1.72—1.90 Å) respectively,[5] where O$_W$, H$_W$, and O$_F$ represent the oxygen and hydrogen atoms of the water molecule and the oxygen atom of the formate group respectively. This indicates that the interaction between the copper formate and the crystalline water layers are similar to the interaction between the copper and the formate group, or to that between the water molecules, so that the bands due to the vibrations, $\nu_b$ and $\nu_c$ in Fig. 7 can be expected not to appear below 100 cm$^{-1}$. The bands due to $\nu_e$ and $\nu_f$ are expected to have lowest frequency. $\nu_f$ is active in the antiferroelectric phase, but inactive in the paraelectric phase, because the wave vector of the vibration is zero in the former phase, but $\pi$ in the latter phase. It can be concluded from the above considerations that the band at 42 cm$^{-1}$, which appears only in the antiferroelectric phase, may be assigned to $\nu_f$, and the band at 62 cm$^{-1}$ to $\nu_e$.

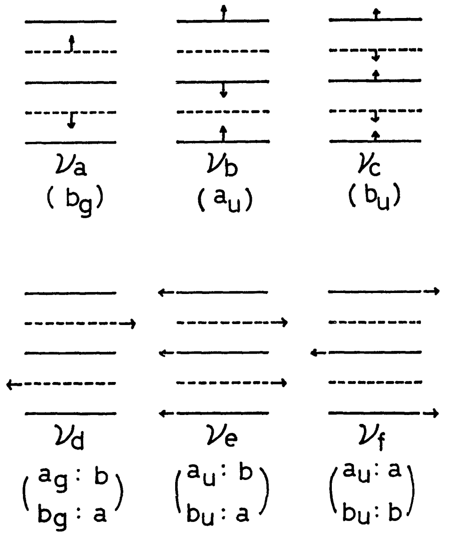

Fig. 7. Vibrations due to the acoustic modes of each layer in the antiferroelectric phase. Bravais unit cell consists of four layers, two of copper formate layer (solid line) and two of H$_2$O layer (dashed line). Symmetry species of each vibration is given in parenthesis. $a_g$: $b$ represents that symmetry species of the vibration, the displacement coordinate of which is along $b$ axis, is $a_g$.

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13) Y. Makita and I. Seo, *J. Chem. Phys.*, **51**, 3058 (1969).