D/H fractionation factor between water vapor and crystal water of copper chloride dihydrate:
Statistical mechanical approach based on Raman spectra

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The D/H fractionation factor between crystal water in copper chloride dihydrate and water vapor was calculated from Raman spectral data for single crystals of CuCl₂·2H₂O and CuCl₂·2D₂O based on statistical mechanics. Single crystals of CuCl₂·2H₂O and CuCl₂·2D₂O were synthesized from supersaturated solutions of pure H₂O and 99.75% D₂O at 25°C. The calculations were made for 25°C using the reduced partition function ratio (RPFR) for gaseous equilibrium, which was assumed to be valid for crystal water-water vapor system in equilibrium. Published H₂O and D₂O spectroscopic data were used to calculate the RPFR for water vapor molecules.

The D/H fractionation factor calculated using the 22 observed vibrational frequencies was 0.936, which is less than the experimental value of 0.999 ± 0.002 by about 6%. Including estimations of the two unobserved librational frequency ratios, the calculated value became 1.014, which is closer to the experimental value, indicating that contribution of librations is not negligible, though smaller than that of the stretching and bending vibrations.

INTRODUCTION

The D/H ratio in hydrous minerals provides useful information regarding hydrogen isotope fractionation, which is governed by the chemical species, structure, and temperature of the crystallized hydrous minerals. The isotopic fractionation factor in hydrous minerals-water systems in equilibrium is essential to elucidating such information. In natural systems, hydrous minerals may exhibit a high degree of hydrogen isotope fractionations. It is known experimentally that the D/H ratio of crystal water and OH groups in hydrous minerals is usually lower than that of the saturated aqueous solution in equilibrium (e.g., Barrer and Denny, 1964; Matsuo et al., 1972; Suzuoki and Epstein, 1976; Sakai and Tsutsumi, 1978; Graham and Sheppard, 1980; Graham et al., 1980; Satake and Matsuo, 1984; Pradhananga and Matsuo, 1985; Horita, 1989; Venneman and O’Neil, 1996; Chacko et al., 1999).

In the concurrent paper (Kakiuchi, 2001), the experimental evaluation of the D/H fractionation factor between crystal water in a copper chloride dihydrate and water vapor is reported. Copper chloride dihydrate exhibits high degree of hydrogen isotope fractionation, primarily attributable to the behavior of the coordination bond between divalent cupreous ions and oxygen atoms in water molecules and hydrogen bond between crystal water and chlorine ions. And the fractionation factor between the crystal water of hydrate and water vapor, which was proposed instead of the fractionation factor between crystal water and the mother liquor, is shown to be a scale worth considering when interpreting the hydrogen and oxy-
gen isotope fractionation in crystalline hydrate-water systems.

Theoretical calculation of the D/H fractionation factor in crystal water-water vapor systems may provide fundamental information concerning D/H fractionation in natural hydrous mineral-water systems. In this study, the authors have attempted to calculate the D/H fractionation factor for a copper chloride dihydrate-water vapor system on the basis of statistical mechanics.

Statistical mechanics, through the application of a reduced partition function ratio (RPFR), has already been successively used to estimate isotopic fractionation factors for systems of gaseous molecules (e.g., Bigeleisen and Mayer, 1947; Urey, 1947). However, for systems containing condensed phases, application of statistical mechanical methods is difficult due to the complexity of interactions between atoms and molecules. However, a number of attempts have been made to calculate the RPFR for liquid or crystalline phases based on rough approximation (e.g., McCrea, 1950; Bottinga, 1968; O’Neil et al., 1969; Shiro and Sakai, 1972; Kakihana et al., 1977). Precise calculation of the RPFR for crystalline phase in hydrous mineral-water vapor systems is prohibitively difficult due to the complexity of interactions between crystal water and atoms in the solid phase. Copper chloride dihydrate is used in this study to calculate the D/H fractionation factor between crystal water and water vapor for the following reasons: (1) Copper chloride dihydrate has a small number of constituent atoms. The crystal structure is relatively simple, and all water molecules in the crystal occur in the same configuration. (2) The coordination bond between one cupreous divalent ion and two water molecules is considerably stronger than the interactions between water molecules and other atoms. (3) Accurate calculation of the D/H fractionation factor will provide an important contribution to the transition metal geochemistry of low-temperature processes. The calculation is performed using the RPFR equation for gaseous equilibrium, giving a first order approximation.

**EXPERIMENTAL**

**Basic equations**

The fractionation factor between crystal water in a hydrous mineral and water vapor, $\alpha_{CW-V}$, is defined as:

$$\alpha_{CW-V} = \frac{(D/H)_{CW}}{(D/H)_{V}}$$

where the subscripts CW and V denote crystal water and water vapor, respectively.

In the case of copper chloride dihydrate, the hydrogen isotope exchange reaction between the crystal water and water vapor is given by:

$$(1/4)\text{CuCl}_2\text{H}_2\text{O}(CW) + (1/2)\text{D}_2\text{O}(V) \rightleftharpoons (1/4)\text{CuCl}_2\text{D}_2\text{O}(CW) + (1/2)\text{H}_2\text{O}(V).$$

The equilibrium constant $K$ for this reaction can be written as:

$$K = \frac{[(Q_{D}/Q_{H})_{CW}]^{1/4}}{[(Q_{D}/Q_{H})_{V}]^{1/2}}$$

where $Q'$ is the partition function of the water molecules, representing the sum of allowable energies.

The equilibrium constant $K$ can then be calculated as the reduced partition function ratio, RPFR ($Q_{D}/Q_{H}$), for a simplified partition function $Q$, given in terms of vibrational energy alone. In Urey (1947) and Bigeleisen and Mayer (1947), $Q_{D}/Q_{H}$ is expressed by $f$, and defined as:

$$f = Q_{D}/Q_{H} = (Q'_{D}/Q'_{H})(m_{H}/m_{D})^{3/2}$$

where $m$ denotes the molecular weight. Here,

$$\frac{Q_{D}}{Q_{H}} = \frac{\sigma_{H}}{\sigma_{D}} \prod_{i=1}^{N} \frac{U_{Di}}{U_{Hi}} \left[ \exp\left(-\frac{U_{Hi}}{2}\right) \right] \left[ 1 - \exp\left(-\frac{U_{Hi}}{2}\right) \right]$$

for nonlinear polyatomic molecules such as water. In Eq. (5), $\sigma$ denotes the symmetry number,
and \( U_i \) represents \( \hbar \nu/kT \), where \( \hbar \) is Plank’s constant, \( k \) is Boltzmann’s constant, \( T \) is absolute temperature, and \( \nu_i \) is the vibrational frequency of the molecule on the harmonic approximation. In the solid phase, there are 3N degrees of freedom for a unit cell composed of N atoms.

In order to calculate the RPFR using Eq. (5) from the vibrational frequency data obtained by infrared or Raman spectroscopy, we define the RPFR discretely for each \( i \)-th mode \( f_i \) corresponding to the \( i \)-th frequency mode, given by:

\[
f_i = \frac{(U_D/U_H)[\exp(-U_D/2)/[1 - \exp(-U_D)]]}{\exp(-U_H/2)}.
\]

The RPFR in Eq. (4) can be calculated as the product of all \( f_i \) values.

The equilibration constant in Eq. (2) gives the D/H fractionation factor between crystal water in copper chloride dihydrate and water vapor \( \alpha_{CW-V} \), assuming that the RPFR between HDO and H\(_2\)O molecules corresponds to the geometric mean of the RPFR between D\(_2\)O and H\(_2\)O molecules in the vapor and crystal phases. This assumption is generally accepted (e.g., O’Neil, 1986; Kakiuchi, 1994; Criss, 1999), however strictly speaking, the equilibrium constants of the reaction, H\(_2\)O + D\(_2\)O = 2HDO, in vapor and condensed phases differ slightly by a few permil (Kakiuchi, 2000). Then,

\[
K = \alpha_{CW-V}.
\]

**Results and Discussion**

Crystal structure and factor group analysis

The crystal structure of copper chloride dihydrate (e.g., Beattie et al., 1969; Fifer and Schiffer, 1969, 1971; Fukushima, 1971; Tanaka et al., 1987) and the internal modes of the water molecules have been thoroughly characterized. However, there remains some ambiguity regarding the positions of lower wavenumber bands and their assignments.

Raman measurements were performed on a SPEX 1403 double monochrometer. The spectra were obtained with a spectral slit width of 3.6 cm\(^{-1}\). The 514.5 nm light of an NEC GLG-3250 Ar-ion laser was used as the excitation source at 40 to 150 mW. The spectra were recorded using a Hamamatsu R649 photomultiplier in combination with a conventional photon-counting system. In order to verify the band wavenumbers, the H\(_2\)O and D\(_2\)O spectra of single crystals were measured at 86 and 88K, regulated by an Oxford DN-1704 cryostat. The specimens were mounted in a dry nitrogen atmosphere, and the sample temperature was measured using a chromel-alumel thermocouple (Nakayama and Ishii, 1987). The spectra of single crystals were measured under several polarization conditions.

**Fig. 1. Crystal structure of copper chloride dihydrate (Peterson and Levy, 1957).**
drate, first determined by neutron diffraction in a study by Peterson and Levy (1957), is shown in Fig. 1. In the crystal, a single copper atom is bonded to two oxygen atoms of water molecules at 1.93Å, and to two chlorine atoms at 2.28Å; i.e., the bond lengths of a metal-oxygen bond in CuCl₂H₂O are slightly different to those of a metal-chlorine bond. As shown in Fig. 1, two water molecules and two chlorine ions are bonded as ligands by metal-oxygen bonds and metal-chlorine bonds in the plane. It was found that the whole system CuCl₂H₂O is coplanar, including the H atoms, and that the H atoms nearly lie along the straight line joining oxygen atoms of water molecules to their two nearest chlorine neighbors.

There are 54 modes for 18 atoms of a unit cell of copper chloride dihydrate. In order to assign the vibrational spectra, factor group analysis for two CuCl₂H₂O molecules for a unit cell was performed. The results are given in Table 1. Three of these modes are low-energy acoustic modes that relate to sound velocity; the other modes correspond to optical lattice and intramolecular vibrations of copper chloride dihydrate. We were able to identify 22 modes of the 24 theoretical Raman active modes for this crystal (i.e., 12 translations, 6 librations and 6 intramolecular vibrations), which is in good agreement with the literature (Beattie et al., 1969).

### Table 1. Factor group analysis of single crystal of copper chloride dihydrate (two molecules in unit cell)

<table>
<thead>
<tr>
<th></th>
<th>D₂ₙ</th>
<th>tot.</th>
<th>acous.</th>
<th>trans.</th>
<th>lib.</th>
<th>vib.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>6</td>
<td>0</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>x², y², z² Raman Active</td>
</tr>
<tr>
<td>B₁₈</td>
<td>6</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>xy Raman Active</td>
</tr>
<tr>
<td>B₂₉</td>
<td>6</td>
<td>0</td>
<td>3</td>
<td>1</td>
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<td>xz Raman Active</td>
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<td>0</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>yz Raman Active</td>
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</tr>
<tr>
<td>B₄₈</td>
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<td>1</td>
<td>5</td>
<td>2</td>
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<td></td>
</tr>
<tr>
<td>B₅₈</td>
<td>6</td>
<td>1</td>
<td>2</td>
<td>1</td>
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<tr>
<td>B₆₈</td>
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<td>1</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

*tot.: Total number of modes.*
*acous.: Acoustic mode.*
*trans.: Translational mode.*
*lib.: Libration (rotational optical) mode of H₂O molecule.*
*vib.: Intramolecular vibrational mode.*

### Raman spectra

The Raman spectra for a single crystal of CuCl₂H₂O (Cryst.) at 86K, and a saturated solution of copper(II) chloride in pure H₂O (Sol.) and pure liquid H₂O (Water) at room temperature are shown in Figs. 2(a) and (b) for wavenumber ranges of 0 to 1800 cm⁻¹ and 2600 to 3800 cm⁻¹, respectively. The bands for the saturated solution spectra tend to be broader than the bands for the crystal spectra. Furthermore, the bands in the 86K crystal spectrum are sharper than those obtained at room temperature, allowing the wavenumbers of the bands to be identified accurately.

The Raman spectrum for the single crystal of CuCl₂D₂O at 88K in the wavenumber ranges 0 to 1800 cm⁻¹ and 2300 to 2700 cm⁻¹ is shown in Fig. 3.

The wavenumbers of 22 bands in the spectra for the single crystals of the H₂O and D₂O dihydrates of copper chloride are shown in Table 2. The 697 cm⁻¹ band for CuCl₂H₂O and the 518 cm⁻¹ bands for CuCl₂D₂O in the libration (hindered rotation) regions for water molecules are in agreement with the literature (Tanaka et al., 1987), and three other bands in the libration region for CuCl₂H₂O and CuCl₂D₂O were identified. Thus, in the libration modes, the 4 bands of the 6 modes for copper chloride dihydrate were observed. Many of the bands in the lower wavenumber re-
D/H fractionation factor

The three sharp bands in this region were assigned to cations and crystal water in agreement with the Raman data of CuCl\(_2\)\(\cdot\)H\(_2\)O and CuCl\(_2\)\(\cdot\)D\(_2\)O obtained by Beattie et al. (1969).

We considered that the bands observed for CuCl\(_2\)\(\cdot\)D\(_2\)O correspond to those observed for CuCl\(_2\)\(\cdot\)H\(_2\)O. The frequency ratio (wavenumber ratio) of the \(i\)-th mode for CuCl\(_2\)\(\cdot\)H\(_2\)O and CuCl\(_2\)\(\cdot\)D\(_2\)O (\(\nu_H/\nu_D\)), and the assignments are shown in Table 2. The frequency ratios of the 10 bands in the higher wavenumber region \((i = 1 \text{ to } 10)\) are close to the theoretical values, whereas those of the 12 bands in the lower wavenumber region \((i = 11 \text{ to } 22)\) are close to unity. Therefore, the RPFR of the \(i\)-th frequency mode \(f_i\) in this region is close to unity, suggesting that the contribution of the \(f_i\) values in the lower wavenumber region is negligible in the calculation of the RPFR.

The vibration wavenumbers for water vapor used for the calculation of the RPFR, were taken from the literature (Fraley and Narahari Rao, 1969; Murphy, 1977; Gupta, 1981), and are shown in Table 3.
H$_2$O and D$_2$O (Table 2). The band wavenumbers for single crystals obtained at 86K and 88K differ from those obtained at room temperature, however this difference is only slight and was ignored in this study.

The $f_i$ values for the OH stretching mode ($i = 1$ to 4) of water molecules in copper chloride dihydrate were very large in comparison to the bending ($i = 5$ and 6) and libration ($i = 7$ to 10) modes. The remaining $f_i$ values in the lower wavenumber region ($i = 11$ to 22) were close to unity, suggesting that these do not contribute measurably to the RPFR values.

Calculation of reduced partition function ratio

The RPFR of the $i$-th mode in copper chloride dihydrate in Eq. (5'), $f_i$, which was presented in the harmonic approximation, was calculated using the band wavenumbers obtained at 86K for H$_2$O and 88K for D$_2$O (Table 2). The band wavenumbers for single crystals obtained at 86K and 88K differ from those obtained at room temperature, however this difference is only slight and was ignored in this study.

The $f_i$ values for the OH stretching mode ($i = 1$ to 4) of water molecules in copper chloride dihydrate were very large in comparison to the bending ($i = 5$ and 6) and libration ($i = 7$ to 10) modes. The remaining $f_i$ values in the lower wavenumber region ($i = 11$ to 22) were close to unity, suggesting that these do not contribute measurably to the RPFR values.

It is considered possible to calculate the RPFR for the 24 theoretical Raman active modes obtained through the group factor analysis in this study. The 24 modes for the two copper chloride dihydrate molecules in a unit cell represent about

Table 2. Band positions $\omega_i$ and frequency ratios of $i$-th mode ($\nu_i/\nu_D$), for H$_2$O and D$_2$O in single crystals of copper chloride dihydrate, and calculated RPFR values of $i$-th mode in Eq. (5'), $f_i$, and assignments

<table>
<thead>
<tr>
<th>$i$</th>
<th>$\omega_i$ (cm$^{-1}$)</th>
<th>($\nu_i/\nu_D$)$_i$</th>
<th>RPFR ($f_i$)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCl$_2$H$_2$O</td>
<td>CuCl$_2$D$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3391</td>
<td>2534</td>
<td>1.338</td>
<td>5.9091</td>
</tr>
<tr>
<td>2</td>
<td>3381</td>
<td>2505</td>
<td>1.350</td>
<td>6.1336</td>
</tr>
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<td>3</td>
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<td>6.1507</td>
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<tr>
<td>4</td>
<td>3351</td>
<td>2461</td>
<td>1.362</td>
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<tr>
<td>5</td>
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<td>1201</td>
<td>1.352</td>
<td>2.0576</td>
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<tr>
<td>6</td>
<td>1611</td>
<td>1195</td>
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<td>7</td>
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<td>585</td>
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<td>697</td>
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<td>1.0008</td>
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<td>22</td>
<td>61</td>
<td>59</td>
<td>1.034</td>
<td>1.0002</td>
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</table>

*Beattie et al. (1969).

Table 3. Vibration wavenumbers for H$_2$O and D$_2$O in vapor phase, and frequency ratios $\nu_i/\nu_D$ and $f_i$ values in Eq. (5) for $\nu_1$, $\nu_2$, and $\nu_3$ vibrations

<table>
<thead>
<tr>
<th>Band</th>
<th>$\omega$ (cm$^{-1}$)</th>
<th>$\nu_i/\nu_D$</th>
<th>RPFR ($f_i$)</th>
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<tr>
<td>H$_2$O</td>
<td>D$_2$O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_1$</td>
<td>3657.05*1</td>
<td>2672.811*2</td>
<td>1.3682</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>1594.747*3</td>
<td>1178.374*2</td>
<td>1.3533</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>3755.97*4</td>
<td>2787.718*3</td>
<td>1.3473</td>
</tr>
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</table>

*1Fraley and Narahari Rao (1969); *2Murphy (1977); *3Gupta (1981).
half of the total of 54 modes and can be considered roughly equivalent to the numbers of modes for one copper chloride dihydrate molecule in a unit cell. In this study, phonon dispersion in the crystal was ignored in the calculation of the RPFR.

The $f_i$ values for water vapor were calculated using the reliable infrared data for the OH stretching mode ($\nu_1$ and $\nu_3$ bands) obtained by Fraley and Narahari Rao (1969). Raman data for the bending mode ($\nu_2$ band) by Murphy (1977) for H$_2$O, and infrared data by Gupta (1981) for D$_2$O. The vibration wavenumbers for H$_2$O and D$_2$O in vapor phase, the frequency ratios, and the RPFR for the $\nu_1$, $\nu_2$, and $\nu_3$ modes are shown in Table 3.

The RPFR of copper chloride dihydrate was calculated for the 6 vibrational frequencies (the stretching and bending modes), the 10 frequencies (the stretching and bending modes and the 4 detected librational modes), and all the obtained frequencies (22 bands). The results are shown in Table 4, along with the RPFR of water vapor, calculated for the product of the $f_i$ values in copper chloride dihydrate and the $f_i$ values in water vapor using Eq. (5'). The calculated ratios are shown in Table 4. The ratio calculated using only 6 vibration frequencies ($i = 1$ to $6$) of copper chloride dihydrate in the second column, 0.792, was significantly smaller than that calculated by the 6 vibration and 4 libration frequencies ($i = 1$ to $10$) in the third column, 0.930. This indicates that the contribution of the librational frequencies of water molecules is significant. Taking the 22 observed bands for H$_2$O and D$_2$O in copper chloride dihydrate into account, the calculated value in the fourth column, 0.936, approaches the experimental value. Although the contribution of the bands at lower wavenumbers ($i = 11$ to $22$) is thought to be negligible, there is still a difference of about 6%. This may be the limit to the accuracy of the calculation of the fractionation factor using the frequencies of copper chloride dihydrate obtained in this study.

In order to approach to the experimental value, $\alpha_{\text{CW-V}} = 0.999$, we need to estimate the frequency ratio of the two undetected libration modes. The $f_i$ values for the four detected bands in the libration region were averaged. Then, the estimated RPFR for the 24 Raman activities of copper chloride dihydrate was obtained to be 11.21, giving a fractionation factor of 1.014, which is considerably closer to the experimental value. This shows that the contribution of the libration modes is significant, and all modes in the libration region must

<table>
<thead>
<tr>
<th>CuCl$_2$H$_2$O/CuCl$_2$D$_2$O</th>
<th>Vibration (6)</th>
<th>Vibration (6)</th>
<th>Detected total (22)</th>
<th>Raman active (24)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(from $i = 1$ to $i = 6$)</td>
<td>(from $i = 1$ to $i = 10$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$f_i = \prod_i$</td>
<td>5854</td>
<td>11155</td>
<td>11428</td>
<td>15783</td>
</tr>
</tbody>
</table>

**Table 4.** Products of reduced partition function ratios of copper chloride dihydrate and water vapor, ($Q_D/Q_H$)$_{\text{CW}}$ and ($Q_D/Q_H$)$_{\text{V}}$, and estimated fractionation factors between crystal water of copper chloride dihydrate and water vapor $\alpha_{\text{CW-V}}$ at 25°C. Experimental value is $\alpha_{\text{CW-V}} = 0.999 \pm 0.002$ at 25°C (Kakiuchi, 2001)
be detected to allow a more accurate calculation.

The difference between the theoretical and experimental values can be attributed to many of the assumptions made to simplify calculation. However, it can be concluded that it may be possible to estimate the D/H fractionation factor if all the modes, or at least the stretching, bending and libration modes in crystalline hydrates of H$_2$O and D$_2$O, can be measured by Raman spectroscopy.

In conclusion, we have demonstrated a means of calculating the D/H fractionation factor between copper chloride dihydrate and water vapor using the 22 frequencies of H$_2$O and D$_2$O vibration in copper chloride dihydrate and the 3 frequencies of H$_2$O and D$_2$O vibration in water vapor. It was shown that all libration frequencies are necessary in order to calculate the fractionation factor accurately, in addition to the stretching and bending frequencies. This approach, using statistical mechanical techniques to calculate the D/H fractionation factor with vibrational frequencies identified by Raman spectral data, can in principle be applied to the evaluation of D/H fractionation factor between all hydrous minerals and water vapor.

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