Spectral Analysis on the Nickel Hydroxyl and Deuteroxyl Nitrate Powders

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Abstract. Infrared absorption (4000-400 cm$^{-1}$) and Raman (4000-50 cm$^{-1}$) spectra of the magnetic geometrically frustrated compound nickel hydroxyl nitrate (Ni$_2$(OH)$_3$NO$_3$), and incompletely deuterized nickel hydroxyl/deuteroxyl nitrate (Ni$_2$(OH/D)$_3$NO$_3$) powders, which were synthesized successfully by the hydrothermal methods, have been measured at room temperature and analyzed in four spectral regions (the [OH/D] and [NO$_3$] functional group regions, the [OH/D] and [NO$_3$] correlation peak region and the Ni-related fingerprint region) by referring to the spectral assignments of the layered $\beta$-Ni(OH)$_2$ and $\beta$-Ni$_2$(OH)$_3$Cl. The spectral analysis can be beneficial to analyzing their low temperature spectral properties, which can help to understand the underlying physics of their exotic quantum phenomena at low temperatures from the spectroscopic point of view.

Keywords. Spectral analysis, nickel hydroxyl nitrate, nickel deuteroxyl nitrate, infrared spectrum, Raman spectrum.

1. Introduction

Transition metal hydroxyl halides with the chemical formula $M_2$(OH)$_3X$ ($M = $ Mn, Fe, Co, Ni, Cu, and $X = $ Cl, Br, I) have been found to possess unconventional magnetic transitions at low temperatures originated from the geometric frustration property [1-3], and besides the conventional magnetic methods, these quantum magnetic phenomena, such as in $\gamma$-Cu$_2$(OH)$_3$Cl, can be studied by use of the temperature-dependent vibration spectral methods (Raman and mid-IR) because of the spin lattice/phonon coupling effect [4,5]. Therefore the assignment of appearing spectral bands/lines of these inorganic coordination compounds is a fundamental task at room temperature. For a similar but relatively complicated geometric frustration material series where $X = $ NO$_3$, such as Cu$_2$(OH)$_3$NO$_3$, is also investigated in the magnetic respect, and the IR and Raman spectra at room and low temperatures are studied only in the pure spectral aspect [6-8].

As to the nickel hydroxyl nitrate with the molecular formula Ni$_2$(OH)$_3$NO$_3$, like its counterpart Ni$_2$(OH)$_3$Cl [9-11], its IR and Raman spectra at room temperature are surely needed to be studied carefully. Because till now the IR and Raman spectral analysis of Ni$_2$(OH)$_3$Cl is not comprehensive and not completely correct [12], here the IR and Raman spectral analysis of Ni$_2$(OH)$_3$NO$_3$ and its deuteride Ni$_2$(OD)$_3$NO$_3$ is reported by referring to the spectral assignments of the layered Ni$_2$(OH)$_3$NO$_3$ and $\beta$-Ni$_2$(OH)$_3$Cl [13,14], in order to help to understand the underlying physics of their exotic quantum phenomena at low temperatures from the spectroscopic point of view.
2. Experimental methods

The Ni$_2$(OH)$_3$NO$_3$ powder sample was prepared by hydrothermal synthesis method by reference to the β–Ni$_2$(OH)$_3$Cl [10].

The preparation of Ni$_2$(OD)$_3$NO$_3$ sample is slightly more complicated. Ni(NO$_3$)$_2$·6H$_2$O powder was first dehydrated in drying oven for two days at 60 °C. The incompletely dehydrated Ni(NO$_3$)$_2$ (1.827 g, 0.01 mol) was dissolved into the heavy - water (deuterioxide, 10 ml) and 30 wt% NaOD-D$_2$O solution (0.41 g, 0.01 mol NaOD in the 1.366 g solution) was diluted by 5 ml heavy – water. Then the diluted NaOD-D$_2$O solution was gradually dropped into the Ni(NO$_3$)$_2$·D$_2$O solution and the flocculation-like precipitate Ni$_2$(OD)$_3$NO$_3$ was gradually generated. The precipitate Ni$_2$(OD)$_3$NO$_3$·D$_2$O solution was put into a sealed reaction vessel and kept at 100 °C for one day. After a filtration process and a dry procedure for one day at 60 °C, the Ni$_2$(OD)$_3$NO$_3$ powder was obtained. In fact the powder was incompletely deuterized, therefore the sample was written as Ni$_2$(OH/D)$_3$NO$_3$ ever after.

The thermogravimetry (TG) curves at 40 °C - 600 °C were obtained by the TG209F3 Tarsus (Netzsch, Germany) with increasing temperature speed 10 K/min.

The IR spectra were measured with Nicolet iS50 (Thermo Fisher, USA) FTIR spectrometer whose measurement region was between 4000 - 400 cm$^{-1}$, by using of the general KBr disc technology.

Raman spectra were obtained using XploRA PLUS Laser confocal micro-Raman microscopy (Horiba, Japan) excited by an Nd: YAG laser (532.0 nm) with the 1200 g/mm grating between 4000 – 50 cm$^{-1}$. The Raman spectrum was automatically baseline corrected (fluorescence subtracted partly), moderately smoothed and normalized according to the largest counting peak value.

3. Results and Discussion

Figure 1 shows the TG curves of Ni$_2$(OH)$_3$NO$_3$ and Ni$_2$(OH/D)$_3$NO$_3$ samples at 40 °C-600 °C.

![Graph](image)

**Figure 1.** Thermogravimetry curves of Ni$_2$(OH)$_3$NO$_3$ and Ni$_2$(OH/D)$_3$NO$_3$.

From the following thermal decomposition equation (1), one can determine that Ni$_2$(OH)$_3$NO$_3$ sample is almost pure, because the weight percentage at 600 °C is 66.0 % that is very close to the theoretical 64.8 % at > 800 °C.

$$\text{Ni}_2(\text{OH/D})_3(\text{NO}_3) \xrightarrow{>800^\circ C} 2\text{NiO} + \text{others}$$

Equation (1)

230.4 / 233.4 (100%) $\xrightarrow{>800^\circ C}$ 149.4 (64.8/64.0 %) + 81/84 (35.2/36.0 %)

Theoretically the weight percentage of Ni$_2$(OD)$_3$NO$_3$ sample at 600 °C should be about 64.0 %, but from figure 1, the weight percentage is high to 77.4 % and thermal decomposition are conducted by two
steps at about 100 °C and 240 °C. According to following thermal decomposition equation (2) of Ni(OH)2 and Ni(OH)2, which gives the weight percentage of 80.6/78.9 % at >300 °C:

\[
\text{Ni(OH/D)}_2 \xrightarrow{>300 \degree C} \text{NiO} + \text{H}_2\text{D}_2\text{O}
\]

92.7/94.7 (100%) \xrightarrow{>300 \degree C} 74.7 (80.4/78.9 %) + 18/20 (19.6/21.1 %)

The Ni2(OH/D)3NO3 sample may also contain some Ni(OH)2 and Ni(OH)2.

Figures 2a and 2b show their IR and Raman spectra in the ranges of 4000-400 cm⁻¹, and 4000-50 cm⁻¹, respectively.

![Figure 2. IR (a) and Raman (b) spectra of Ni2(OH)3NO3 and Ni2(OH/D)3NO3 samples.](image)

According to the general spectral analysis method, both IR and Raman spectra can be divided into four regions: [OH/D] and [NO3] functional group (FG1 and FG2 regions), [OH/D] correlation peak (CP) region, and fingerprint (FP) region, see figures 3-6, respectively. In the spectral analysis process, we will refer to the well-established crystal structure information, the analysis results of the β-Ni(OH)2 [12], Ni2(OH)3NO3 [13], and β-Ni2(OH)3Cl [14], and other experiences.

[OH/D] FG region (4000-2000 cm⁻¹). Theoretically, according to the biatomic vibration frequency’s formula, the redshift rate of the [OD] stretching modes relative to the [OH] one is estimated to be [(16x1/(16+1)) / (16x2/(16+2))]¹/² = 72.76 %. From figure 3a, only one IR main band is observed at 3625 cm⁻¹ for Ni2(OH)3NO3, which belong to a stretching vibration normal mode ν(OH) affected by a very small hydrogen bond effect. Correspondingly, one IR main band of Ni2(OH/D)3NO3 is observed at 2680 cm⁻¹, which is 73.93 % of IR ν(OH) and therefore is obviously ν[OD]. Moreover, ν(OH) at 2680 cm⁻¹, ν(H2O) at ca. 3400 cm⁻¹, and ν(D2O) at ca. 2430 cm⁻¹ are also observed in the IR spectrum of Ni2(OH/D)3NO3, which demonstrate that the sample is really incompletely deuterized and some H₂O and D₂O remain unavoidably as predicted in the sample. As to the Raman spectra shown in figure 3b, three bands (3653, 3635 and 3584 cm⁻¹) belonging to ν(OH) are observed for Ni2(OH)3NO3, while for Ni2(OH/D)3NO3, two bands (2659 and 2647 cm⁻¹) surely belonging to ν[OD] appear and two bands (3600 and 3584 cm⁻¹) are also observed to mean that the sample is really incompletely deuterized.

[NO3] FG region (2000-1000 cm⁻¹). From figures 4a and 4b, for Ni2(OH)3NO3, one can see that two strong IR/Raman main bands at 1501/1518 and ca.1284/1296 cm⁻¹ are observed as expected, which are ascribed both IR and Raman active antisymmetric stretching mode ν(NO3) (νI) and symmetric stretching mode ν(NO3) (νI). But for Ni2(OH/D)3NO3, two strong IR main bands redshift to ca.1400 and 1339 cm⁻¹, while two well-separated Raman bands appear at 1386 and 1067 cm⁻¹, which show the possible strong hydrogen bond effect by the remnant H₂O and D₂O.
Figure 3. (a) IR spectra and (b) Raman spectra in the range of 4000-2000 cm\(^{-1}\) (hydroxyl/deuteroxyl stretching vibration \(\nu_{\text{1-2}}\)[OH/D]: [OH/D] functional group (FG) region).

Figure 4. (a) IR spectra and (b) Raman spectra in the range of 2000-1000 cm\(^{-1}\) (nitrate radical normal vibration \(\nu_{\text{3-4}}[\text{NO}_3]^{-}\): [NO\(_3\)] functional group (FG) region).

[N\(_2\)(OH)] and [OH/D] CP region (1000-600 cm\(^{-1}\)). According to the normal mode analysis on two correlation peak modes of the [NO\(_3\)] unit, symmetric bending mode \(\nu_2[\text{NO}_3]\) at about 810 cm\(^{-1}\) is only IR active, and out-of plane bending mode \(\nu_3[\text{NO}_3]\) at about 720 cm\(^{-1}\) is both IR and Raman active. From figure 5a and 5b, for Ni\(_2\)(OH)\(_3\)NO\(_3\), \(\nu_2[\text{NO}_3]\) at 800/810 cm\(^{-1}\) and \(\nu_3[\text{NO}_3]\) at 710/716 cm\(^{-1}\) in IR/Raman spectra are observed, and IR/Raman band at 985/988 cm\(^{-1}\) is surely assigned to the correlation peak mode \(\delta[\text{NiOH}]\). The broad band at 645 cm\(^{-1}\) is assigned to be \(\delta[\text{HO}_2]\) because it disappears in Raman spectrum for the laser heating effect. As for Ni\(_2\)(OH/D)\(_2\)NO\(_3\), only one IR/Raman main band at 834/725 720 cm\(^{-1}\) is observed, which is suggested to be \(\delta[\text{NiOD}]\).
can see that its preparation process should be well improved in the existing viewpoint that the Cl atomic quantity is roughly equivalent to that of [NO₃] unit, there maybe three sets of complicated IR/Raman modes: (1) \( v[NiO_3], v[NiO_3], v[NiO_5(NO_3)] \) and \( v[NiO_5(NO_3)] \) units in the range of 600-300 cm\(^{-1} \), (2) lattice vibration modes \( v_{\text{lattice}} \) in the range of 300-200 cm\(^{-1} \), and (3) \( v[Ni(OH)] \) with the wavenumbers of less than 200 cm\(^{-1} \). In figures 6a and 6b, the IR bands at 521/500 cm\(^{-1} \) and 481/418 cm\(^{-1} \), which originate from those [Ni-O] related modes (unanimously called \( v[Ni-O] \)), for two samples are observed. For Ni₂(OH)₃NO₃, Raman bands 468 cm\(^{-1} \) (\( v[Ni-O] \)), 248/225 cm\(^{-1} \) (\( v_{\text{lattice}} \)) and 176/122/62 cm\(^{-1} \) (\( v[Ni_3(NO_3)] \)) are observed, but for Ni₂(OH/D)₃NO₃ only 188/101 cm\(^{-1} \) (\( v[Ni_3(NO_3)] \)) appear in the Raman spectrum, which can not be explained by us till now.

Table 1 collects the IR and Raman data of two samples with listing the suggested assignment and the published spectral data of Ni₂(OH)₃NO₃ [13] and \( \beta-Ni_2(OH)_3Cl \) [14] as assigning references.

**4. Summary**

We have prepared and measured infrared and Raman spectra of the nickel hydroxyl and deuterohydroxyl nitrate Ni₂(OH)₃NO₃ to find out its whole really existing vibration spectral bands. Except for two hydroxyl stretching modes \( v_1[OH] \) affected by different hydrogen bonds and corresponding correlation modes \( \delta [NiOH/D] \), normal vibration modes \( v_1, v_3, v_4[NO_3] \), \( [Ni-O] \) related modes \( v[Ni-O] \), lattice vibration modes, and \( v[Ni_3(NO_3)] \) modes are observed and tentatively assigned. But from the measurement of thermogravimetry curve and IR/Raman spectra of Ni₂(OH/D)₃NO₃, one can see that its preparation process should be well improved in the dehydration, reaction and drying methods.
Table 1. IR/Raman spectral data (cm$^{-1}$) of Ni$_2$(OH)$_3$Cl with those of β-Ni$_2$(OH)$_3$ and β-Ni$_2$(OH)$_3$Cl as assigning references (only strong or some moderately strong spectral lines are considered).

|                | Ni$_2$(OH)$_3$NO$_3$ | Ni$_2$(OH/D$_2$)NO$_3$ | Ni$_2$(OH)$_3$NO$_3$ [13] | β-Ni$_2$(OH)$_3$Cl [14] |
|----------------|----------------------|------------------------|---------------------------|-------------------------|
| IR/Raman Assign. | 3635/3635 ν$_{v4}$[OH] | 3625 ν$_{v4}$[OH] | 3593/3587 ν$_{v4}$[OH] | 3577/3577 ν$_{v2}$[OH] |
| [OH] FG         | [3625/3635 ν$_{v4}$[OH]] | [3625 ν$_{v4}$[OH]] | [3593/3587 ν$_{v4}$[OH]] | [3577/3577 ν$_{v2}$[OH]] |
| [OD] FG         | 2680/2659 ν$_{v1}$[OD] | 2657/2675 ν$_{v1}$[OD] | 2692/2675 ν$_{v1}$[OD] | 2692/2675 ν$_{v1}$[OD] |
| [NO$_3$] CP     | 879/897 ν$_{v3}$[NO$_3$] | 803 ν$_{v3}$[NO$_3$] | 746/758 δ[NO$_3$] | 692/693 δ[NO$_3$] |
|                | 500/500 ν$_{v4}$[NO$_3$] | 482 δ[NO$_4$][OH] | 456/451 ν$_{v4}$[NO$_3$] | 448/442 ν$_{v4}$[NO$_3$] |
|                | 418/418 ν$_{v5}$[NO$_3$] | 390 δ[NO$_4$][OH] | 437/437 ν$_{v5}$[NO$_3$] | 421/421 ν$_{v5}$[NO$_3$] |
|                | 237 ν$_{v4}$[NO$_3$] | 201 ? | 201 ? | 201 ? |
|                | 404/404 ν$_{v4}$[NO$_3$] | 365/375 ν$_{v4}$[NO$_3$] | 351/351 ν$_{v4}$[NO$_3$] | 351/351 ν$_{v4}$[NO$_3$] |
| [Ni-O] FP       | 289 ν$_{v4}$[NO$_3$] | 289 ν$_{v4}$[NO$_3$] | 289 ν$_{v4}$[NO$_3$] | 289 ν$_{v4}$[NO$_3$] |
| [Ni-O] FP       | 418/418 ν$_{v5}$[NO$_3$] | 390 δ[NO$_4$][OH] | 437/437 ν$_{v5}$[NO$_3$] | 421/421 ν$_{v5}$[NO$_3$] |
| [Ni-O] FP       | 237 ν$_{v4}$[NO$_3$] | 201 ? | 201 ? | 201 ? |

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