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# A NEW SIMPLE ROUTE FOR SYNTHESIS OF CADMIUM(II), ZINC(II), COBALT(II), AND MANGANESE(II) CARBONATES USING UREA AS A CHEAP PRECURSOR AND THEORETICAL INVESTIGATION

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**ABSTRACT**. The $MnCO_3.H_2O$, $CoCO_3.4H_2O$, $ZnCO_3$, and $CdCO_3$, respectively, were synthesized through a new precise, easy pathway for the reaction of $MnI_2$, $CoI_2$, $ZnI_2$, or $CdI_2$ aqueous solutions with a cheap precursor-urea for 10 h at ~ 70 ºC. The IR spectra of reaction products designate the presence of characteristic bands of ionic carbonate, $CO_3^{2-}$ and absence of the individual bands of urea. The $(CO_3)^{2-}$ ion is planar and therefore, it belongs to the $D_{3h}$ symmetry. It is expected to display four modes of vibrations. The stretching vibrations of the type; ν(C-O) is observed in the range of (1376-1503) $cm^{-1}$ while another stretching vibration ν(C-O) is observed in the region 1060-1079 $cm^{-1}$. The out of plane of vibration δ(OCO) is observed in the range of (833-866) $cm^{-1}$ while, the angle deformation bending vibration δ(OCO) appear in the range of (708-732) $cm^{-1}$. The infrared spectra of metal carbonate, show that, this product clearly has an uncoordinated water. The band related to the stretching vibration ν(O-H) of uncoordinated $H_2O$ is observed as expected in the range of ~ 3000 $cm^{-1}$. A general mechanism explaining the synthesis of carbonate compounds of cadmium(II), zinc(II), cobalt(II), and manganese(II), are described. Moreover, the DFT outcomes using B3LYP/LanL2DZ (basis set) agree with the experimental results.

**KEY WORDS**: Carbonate, $CoI_2$, Infrared spectra, Urea, DFT

## INTRODUCTION

The importance of urea ($NH_2CONH_2$) in the human body cannot be overstated. It is the most important nitrogenous by-product of the metabolism of protein. The melting point of urea is 132 °C; it is insoluble in ether and soluble in ethanol and water. Fertilizers, barbiturates and resin (plastics) are prepared from urea compounds [1-6]. It is widely used to soften cellulose in the paper industry and is also utilized to enhance infected wound healing and many other medical purposes [7-9]. Metal-urea complexes are employed in pharmaceuticals, such as platinum-urea complex, used as an anticancer agent [10].

All the frequencies observed in the urea-$d_4$ and urea spectra were assigned by Yamaguchi and Stewart [11, 12]. The frequency at 1603 $cm^{-1}$ was assigned for $NH_2$ bending motion and 1686 $cm^{-1}$ for CO stretching. Yamaguchi's calculations revealed that the contribution of $NH_2$ bending motion is higher than that of CO stretching motion for the band at 1686 $cm^{-1}$. $ND_2$ bending vibrations are ascribed to IR bands of urea-d4 found at 1245 and 1154 $cm^{-1}$. The measured depolarization degrees of the Raman lines support this claim. The CN stretching vibration is attributed to the 1464 $cm^{-1}$ frequency of urea, at 1490 $cm^{-1}$ corresponding frequency is observed of urea-$d_4$. $NH_2$ rocking vibrations are attributed to 1150 $cm^{-1}$ band.

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At room temperature, the interactions between urea and transition metal ions [13-17] have been widely explored. IR spectra of such complexes showed that the molecule of urea acts as monodentate ligand, coordinating to metal ions via oxygen atom rather than nitrogen atom.

The reaction products' nature is significantly influenced by the type of metal ions involved, as well as metal salt employed. The novelty in our earlier research was centered on the reaction of various metals like Mo(IV), V(V), Sn(IV), Au(III), Fe(III), Cr(III), Sn(II), Pb(II), and Co(II) with urea ligand [18-27], demonstrating that the type of metal ions, as well as anions, have significant impact on reaction products nature. The reaction of urea with various metal salts at high temperatures resulted in the discovery of a unique method for the preparation of $CoCO_3$ and $PbCO_3$ [21], FeO(OH) [20], lanthanide carbonates [23,27], $SnOCl_2.2H_2O$ [18], $2ZnCO_3.3Zn(OH)_2$ [19], limonite, and oxides ($WO_3$, $MoO_3$, $MnO_2$, and $Cr_2O_3$) due to oxidation reduction between $Na_2WO_4$, $Na_2MoO_4$, $KMnO_4$, and ($K_2CrO_4$ or $K_2Cr_2O_7$), respectively, at ~ 85 °C in aqueous solution with urea [27].

The aim of the present work is to recognize the nature of the reaction products resulted during the reaction of $MnI_2$, $CoI_2$, $ZnI_2$ or $CdI_2$ with urea in aqueous media for 10 h at ~70 °C. Infrared frequencies of all the four metal complexes were calculated theoretically through density functional theory (DFT) to support the experimental results.

## EXPERIMENTAL

### *Preparation and analysis of metal complexes*

The chemicals used in the present work were Analar and extra pure grade. Aqueous solutions (100 mL) of urea (0.1 M) with Cd(II), Zn(II), Co(II), or Mn(II) iodide (0.01 M) was used to prepare the respective $MCO_3.nH_2O$ ($n = 4$ for $CoCO_3$ and $n = 1$ for $MnCO_3$; M = Cd(II), Zn(II), Co(II), or Mn(II)). In a water bath, the solutions were allowed to heat for 10 hours at 70 °C. The resulting solid precipitates were filtered out, washed with hot water multiple times, dried in an oven at 70 °C for 3 hours, and then deposited on silica gel in vacuo. The yields of Cd(II), Zn(II), Co(II), and Mn(II), carbonates produced ranged from 65 to 70%, which depends on the kind of metal and the counter ions linked. By dissolving a sample of each product in excess standard HCl and measuring the excess HCl with standard sodium carbonate [28], the carbonate content of the four compounds was determined. The percentage of cadmium zinc, cobalt, and manganese in the compounds were calculated using a gravimetric technique until a consistent weight and formula were achieved. A Shimadzu FT-IR Spectrophotometer was used to record IR spectra of all reactants, urea, and products in KBr discs.

### *Theoretical calculations*

Package of Gaussian 09Rev software [29] were used for DFT calculations. Gradient corrected correlation with Los Alamos Effective Core Potentials B3LYP/lanL2DZ basis set was employed [30]. The calculated IR frequencies through this method were observed to be positive, which shows that the optimized geometry is at a minimum on the potential energy surface. In the FTIR spectrum, bands that appeared are assigned with full accuracy, using animated modes of vibrations. Computed vibrational wavenumbers are mostly higher than the experimentally obtained values. To establish a good comparison between both vibrational wavenumbers, the scaling factor of 0.9140 is utilized to scale the computed wavenumbers. Gauss View 6.0 software [31] is used to visualize the molecule.

## RESULTS AND DISCUSSION

### *Experimental studies for metal complexes*

Elemental analysis of $MCO_3.nH_2O$ (M = Cd(II), Zn(II), Co(II), or Mn(II)) collected from the reaction of different metal salts with urea is nearly identical, indicating that nitrogen element is absent. Analysis of the solid products obtained are given in Table 1.

Table 1. Elemental analysis of the synthesized metal carbonates of Mn, Co, Zn, and Cd(II) compounds.

| Compounds | MW | Elemental analyses/found (calc.) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | %C | | %H | | %Metal | | % $CO_3^{2-}$ | |
| $MnCO_3.H_2O$ | 132.95 | 8.95 | (9.02) | 1.44 | (1.50) | 41.22 | (41.32) | 45.05 | (45.13) |
| $CoCO_3.4H_2O$ | 190.94 | 6.17 | (6.28) | 4.10 | (4.19) | 30.45 | (30.86) | 31.11 | (31.42) |
| $ZnCO_3$ | 125.38 | 9.48 | (9.57) | -- | -- | 52.08 | (52.14) | 47.77 | (47.85) |
| $CdCO_3$ | 172.42 | 6.89 | (6.96) | -- | -- | 65.11 | (65.19) | 34.62 | (34.80) |

At *Ca.* ~70 °C, reaction of urea aqueous solutions with iodide salts of cadmium(II), zinc(II), cobalt(II), and manganese(II), produces white, red, and brown solid crystalline products, respectively. KBr discs were used to acquire the IR spectra of urea along with reaction products of various cadmium(II), zinc(II), cobalt(II), and manganese(II) salts at high temperatures. Table 2 shows band assignments for the products and Figure 1 shows the IR spectra. IR spectra reveal no bands related to any of the reactants or coordinated urea, but rather a set of bands indicative of ionic carbonate, $(CO_3)^{2-}$ can be seen. [29]. The infrared spectra of commercially obtained $CdCO_3$, $ZnCO_3$, $CoCO_3.nH_2O$, and $MnCO_3.nH_2O$, as well as those derived from elemental analysis data and volumetric determination of the $(CO_3)^{2-}$ group using a standard solution of HCl, are the same as those of the reaction products. The obtained products were successfully identified as $CdCO_3$, $ZnCO_3$, $CoCO_3.4H_2O$, and $MnCO_3.H_2O$. The IR assignments for ionic carbonate $(CO_3)^{2-}$ are quite like those previously reported [32].

According to the previous research [18-27] the nature of obtained reaction product through the reaction of urea and metal ions at high temperature is dependent on the kind of metal ion, as well as metal salts utilized in some cases.

Table 2. Infrared frequencies ($cm^{-1}$) and assignments of the products obtained from the reaction of (a): $MnI_2$, (b): $CoI_2$, (c): $ZnI_2$ or (d): $CdI_2$ with urea at high temperature.

| Frequencies*, $cm^{-1}$ | | | | Assignments |
|---|---|---|---|---|
| a | b | c | d | |
| 2964, 2925 | 2924 | - | 3070, 2954 | ν(O-H); $H_2O$ |
| 1463, 1376<br>1070 | 1464, 1378<br>1079 | 1503, 1391<br>1060 | 1468<br>1077 | ν(C-O); $CO_3^{2-}$ |
| 863<br>726 | 866<br>724,732,722 | 833<br>708 | 860, 836<br>723 | δ(OCO); $CO_3^{2-}$ |

*br, broad; m, medium; sh, shoulder; s, strong; w, weak,ν, stretching; δ, bending.

The coordination compounds of manganese(II) ions with urea have been widely researched at room temperature [33-36], and it was discovered that urea coordinates to Mn(II) ions through its oxygen atom at room temperature, generating the $[Mn(urea)_4]X_2$ octahedral complex [35]. Moreover, $MnU_6X_2$ ($ClO_4^-$ and X = $Br^-$, $I^-$) Mn(II)-urea compounds have also been discovered. They are found to be of ionic nature and could be written as, $[MnU_6]X_2$. The urea is linked to manganese by its oxygen atom in these compounds, which have a high-spin octahedral structure. For understanding the involvement of Mn(II) ions in degrading coordinated urea in the form of $[[Mn(urea)_6]X_2$ or $[Mn(urea)_4]X_2]$ at high temperatures, the following reactions can be used.

The direct decomposition of urea ($NH_2CONH_2$) into $NH_3$ and isocyanic acid (HNCO) and the dissociation of HNCO into $NH_3$ and $CO_2$:

$$NH_2CONH_2 \longrightarrow NH_3 + HNCO$$

$$HNCO + H_2O \longrightarrow NH_3 + CO_2$$

*i- Reaction between $MnI_2$ and urea with 1:4 ratio at room and 70 °C temperatures:*

$$MnI_2 + 4(NH_2CONH_2) + xH_2O \xrightarrow{\text{room Temp.}} [Mn(NH_2CONH_2)_4]I_2 + xH_2O$$

$$[Mn(NH_2CONH_2)_4]I_2 + 6H_2O \xrightarrow{70^oC} MnCO_3.H_2O + 3CO_2 + 2NH_4I + 6NH_3$$

*ii- Reaction between $MnI_2$ and urea with 1:6 ratio at room and 70 °C temperatures:*

$$MnI_2 + 6(NH_2CONH_2) + xH_2O \xrightarrow{\text{room Temp.}} [Mn(NH_2CONH_2)_6]I_2 + xH_2O$$

$$[Mn(NH_2CONH_2)_6]I_2 + 8H_2O \xrightarrow{70^oC} MnCO_3.\ H_2O + 5CO_2 + 2NH_4I + 10NH_3$$

According to the literature [37-39], X-ray investigations on cobalt(II) salt-urea complexes revealed that, $Co(NO_3)^2$ interacts with urea to create the complex, $[Co(urea)_4](NO_3)^2$ at room temperature. Urea coordinates to Co(II) through oxygen atom in these complexes. The following is an explanation of the involvement of Co(II) ions in decomposition of coordinated urea at high temperatures.

*iii- Reaction between $CoI_2$ and urea with 1:4 ratio at room and 70 °C temperatures:*

$$CoI_2 + 4(NH_2CONH_2) + xH_2O \xrightarrow{\text{room Temp.}} [Co(NH_2CONH_2)_4]I_2 + xH_2O$$

$$[Co(NH_2CONH_2)_4]I_2 + 9H_2O \xrightarrow{70\ ^oC} CoCO_3.4H_2O + 3CO_2 + 6NH_3 + 2NH_4I$$

Literature revealed that zinc(II) ion coordination compounds with urea at room temperature [40,41], urea coordinated through its oxygen atom in these complexes, generating the $[Zn(urea)_2X_2]$ complexes, where, X = $CH_3COO^-$, $NO_3^-$, or $Cl^-$. The Zn(II) ions role in degrading urea coordinated in the form of $[Zn(urea)_2X_2$ at high temperatures may be explained as follows;

*iv- Reaction between $ZnI_2$ and urea with 1:2 ratio at room and 70 °C temperatures:*

$$ZnI_2 + 2(NH_2CONH_2) + xH_2O \xrightarrow{\text{room Temp.}} [Zn(NH_2CONH_2)_2I_2] + xH_2O$$

$$[Zn(NH_2CONH_2)_2I_2] + 3H_2O \xrightarrow{70^oC} ZnCO_3 + CO_2 + 2NH_4I + 2NH_3$$

Adducts of $HgX_2$.urea (X = Br, Cl), $CdX_2$·urea (X = I, Br, Cl), $CdX_2$·2urea (X = I, Br), and $ZnX_2$·2urea (X = I, Br, Cl), have been characterized [42]. The stretching vibrations shifted to high (νCN and νNH) and low (νCO) frequencies, indicating that the urea is bonded to oxygen.

The Cd(II) ions role in degrading urea coordinated in the form of $[Cd(urea)_2X_2]$ at high temperatures might be explained as follows;

*vi- Reaction between $CdI_2$ and urea with 1:2 ratio at room and 70 °C temperatures:*

$$CdI_2 + 2(NH_2CONH_2) + xH_2O \xrightarrow{\text{room Temp.}} [Cd(NH_2CONH_2)_2I_2] + xH_2O$$

$$[Cd(NH_2CONH_2)_2I_2] + 3H_2O \xrightarrow{70^oC} CdCO_3 + CO_2 + 2NH_4I + 2NH_3$$

As the $(CO_3)^{2-}$ ion is planar, it corresponded to the $D_{3h}$ symmetry. The Raman active is only vibration A`$_1$, whereas infrared active vibration is $\nu_2$, $\nu_3$ and $\nu_4$, as it should show the four vibration modes, A`$_1$ + A``$_2$ + 2E` (E` is a doubly degenerate motion). In the region ~1070 cm$^{-1}$ the stretching vibration ν(C-O); $\nu_1(A`_1)$ is found as a medium-to-weak band, whereas in the range of 1503-1376 $cm^{-1}$ the stretching vibrations of the type; ν(C-O); $\nu_3(E`)$ is seen as a strong broad band. It must be noted that this motion $(A`_1)$ should be infrared inactive, as evidenced by its weak appearance in the $MCO_3.nH_2O$. This is due to weak solid-solid interactions causes the symmetry of $CO_3^{2-}$ is lower than $D_{3h}$. In the range of 744-708 $cm^{-1}$ the angle deformation bending vibration δ(OCO); $\nu_4(E`)$ is observed as a medium strong, while in the range of ~860 $cm^{-1}$ the out of plane of vibration δ(OCO); $\nu_2(A``_2)$ is seen as a strong band. The IR spectra of metal(II) carbonate, $MCO_3.nH_2O$, reveal that some of these compounds include an uncoordinated water component. In the region of 3000 $cm^{-1}$, the band corresponding to the stretching vibration (O-H) of uncoordinated $H_2O$ is found as predicted (Table 1).

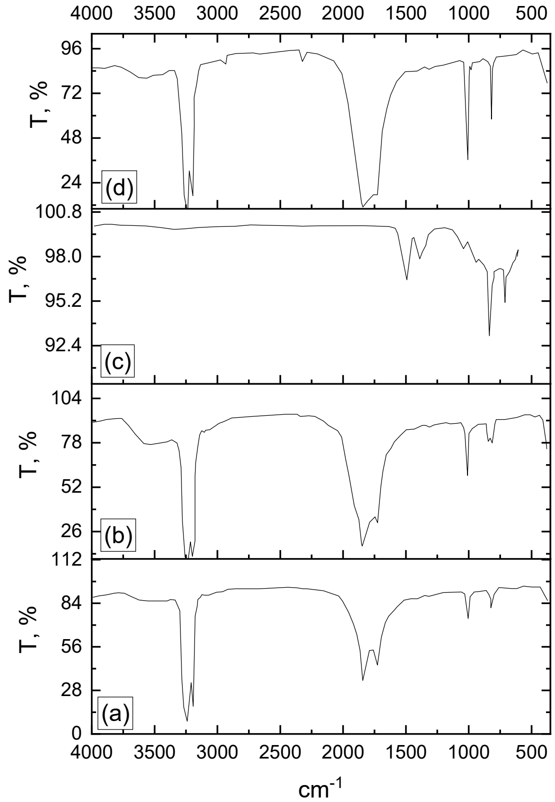

Figure 1. Infrared spectra of the products obtained from the reaction of (a): $MnI_2$, (b): $CoI_2$, (c): $ZnI_2$ or (d): $CdI_2$ with urea at high temperature.

*Computed IR frequencies*

IR frequencies were investigated density functional theory (DFT) using B3LYP/lanL2DZ. Table 3 contains theoretically calculated vibrational, i.e., scaled wavenumbers. The slight difference between theoretical and experimental frequencies is due to theoretical values being acquired in gas phase and experimental values being obtained in solid phase [43]. Therefore, to reduce the differences, the scaling factor 0.9140 is used [44]. The computed IR spectra of all the fore metal complexes are shown in Figures 2-5. For $MnCO_3.H_2O$ a strong peak for ν(O-H) is obtained at

2931 cm$^{-1}$, the peaks at 1558-1546 cm$^{-1}$ are representing C-O stretching, and peaks around 841, 804 cm$^{-1}$ are obtained for δ(O-C-O). Similarly, for $CoCO_3.4H_2O$ a strong peak for ν(O-H) is obtained at 2914 cm$^{-1}$, the peaks at 1563-1547 cm$^{-1}$ are representing C-O stretching, and peaks around 798-753 cm$^{-1}$ are obtained for δ(O-C-O). Computed IR of $ZnCO_3$ and $CdCO_3$, shows C-O stretching at 1556 and 1504 cm$^{-1}$, respectively, and δ(O-C-O) at 750-678 and 762-646 cm$^{-1}$, respectively. These calculated vibrational frequencies vary to a smaller extent from experimental results due to neglecting the incompleteness and anharmonicity of the basis set [45].

Table 3. Assignments theoretical wave numbers of metal complexes with B3LYP/lanL2DZ basis.

| Complex | Unscaled frequency (cm$^{-1}$) | Scaled frequency (cm$^{-1}$) | IR intensity | Assignments |
|---|---|---|---|---|
| $MnCO_3.H_2O$ | 3256, 3187 | 2976, 2913 | 0.9157, 33.3194 | ν(O-H); $H_2O$ |
| | 1704, 1691 | 1558, 1546 | 280.0243, 254.2757 | ν(C-O); $CO_3^{2-}$ |
| | 920, 876 | 841, 801 | 129.9491, 102.0071 | δ(OCO); $CO_3^{2-}$ |
| $CoCO_3.4H_2O$ | 3256, 3188 | 2976, 2914 | 1.0989, 31.0105 | ν(O-H); $H_2O$ |
| | 1710, 1693 | 1563, 1547 | 404.3844, 157.8611 | ν(C-O); $CO_3^{2-}$ |
| | 873, 830, 824 | 798, 759, 753 | 73.4222,78.7248, 317.2646 | δ(OCO); $CO_3^{2-}$ |
| $ZnCO_3$ | 1702 | 1556 | 346.6637 | ν(C-O); $CO_3^{2-}$ |
| | 821, 802, 741 | 750, 733, 678 | 73.4933, 321.4409, 0.0261 | δ(OCO); $CO_3^{2-}$ |
| $CdCO_3$. | 1646 | 1504 | 313.1924 | ν C-O); $CO_3^{2-}$ |
| | 834, 740, 707 | 762, 676, 646 | 61.3913, 290.2409, 8.8775 | δ(OCO); $CO_3^{2-}$ |

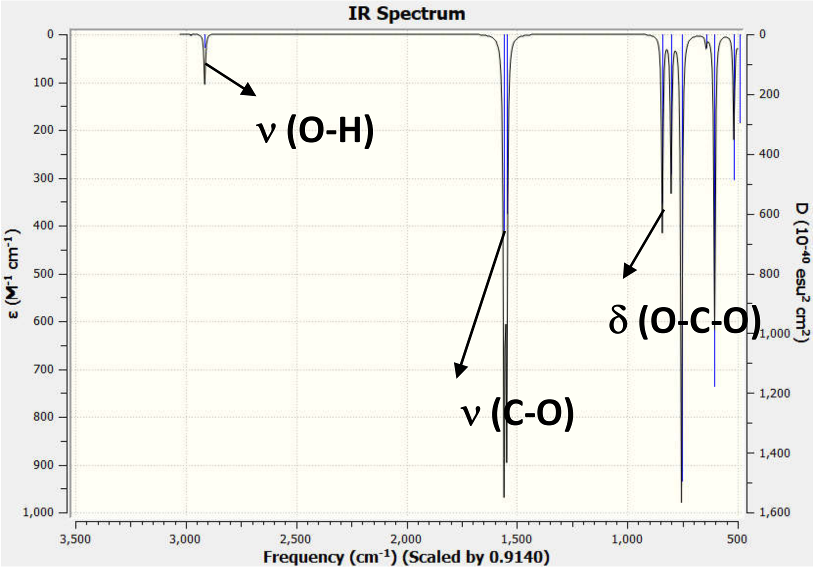

Figure 2. Theoretical IR spectrum of $MnCO_3.H_2O$.

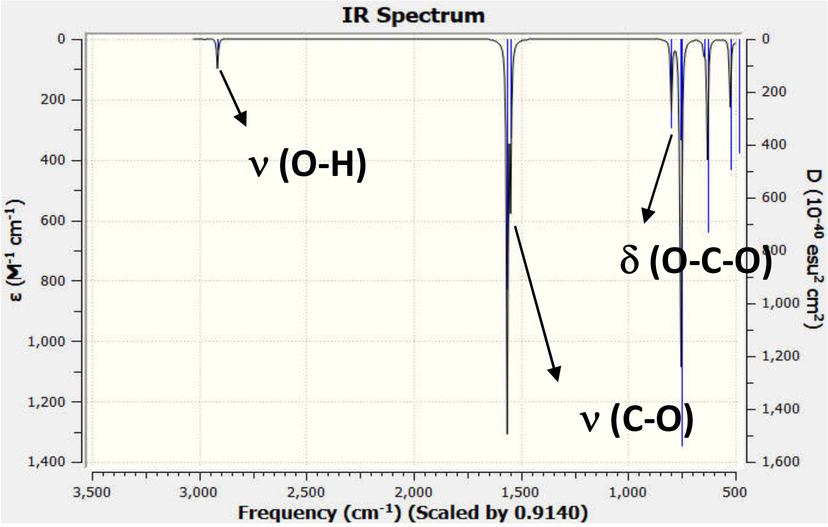

Figure 3. Theoretical IR spectrum of $CoCO_3.4H_2O$.

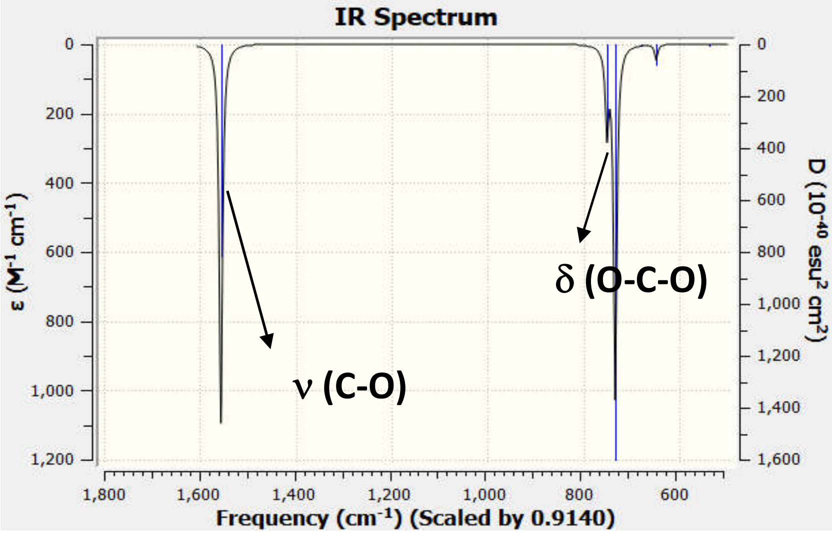

Figure 4. Theoretical IR spectrum of $ZnCO_3$.

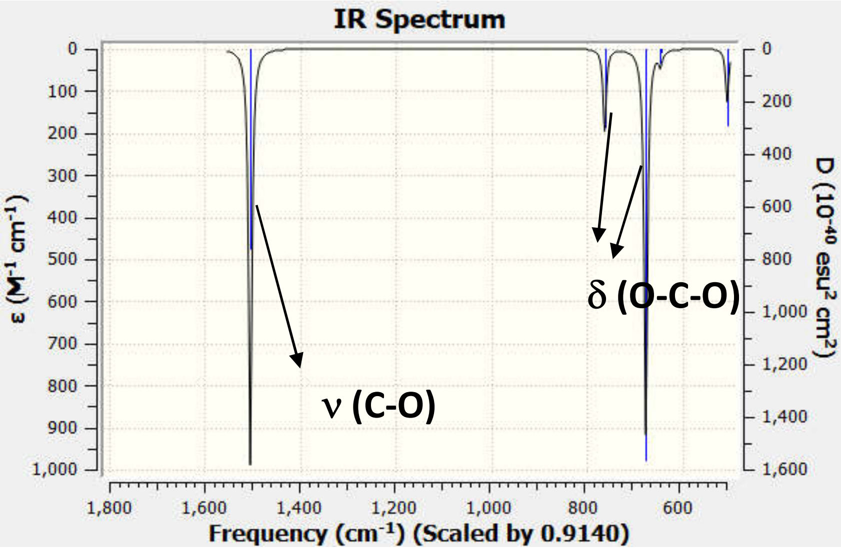

Figure 5. Theoretical IR spectrum of $CdCO_3$.

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