

The effects of librations on the ^{13}C chemical shift and ^2H electric field gradient tensors in β -calcium formate

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The magnitudes and orientations of the principal elements of the ^{13}C chemical shift anisotropy (CSA) tensor in the molecular frame of the formate ion in β -calcium formate is determined using one-dimensional dipolar-shift spectroscopy. The magnitudes of the principal elements of the ^{13}C CSA tensor are $\sigma_{11\text{C}}=104$ ppm, $\sigma_{22\text{C}}=179$ ppm, and $\sigma_{33\text{C}}=233$ ppm. The least shielding element of the ^{13}C CSA tensor, $\sigma_{33\text{C}}$, is found to be collinear with the C–H bond. The temperature dependence of the ^{13}C CSA and the ^2H quadrupole coupling tensors in β -calcium formate are analyzed for a wide range of temperature (173–373 K). It was found that the span of the ^{13}C CSA and the magnitude of the ^2H quadrupole coupling interactions are averaged with the increasing temperature. The experimental results also show that the ^2H quadrupole coupling tensor becomes more asymmetric with increasing temperature. A librational motion about the $\sigma_{22\text{C}}$ axis of the ^{13}C CSA tensor is used to model the temperature dependence of the ^{13}C CSA tensor. The temperature dependence of the mean-square amplitude of the librational motion is found to be $\langle\alpha^2\rangle=2.6\times 10^{-4}(T)\text{ rad}^2\text{ K}^{-1}$. The same librational motion also accounts for the temperature-dependence of the ^2H quadrupole coupling tensor after the relative orientation of the ^{13}C CSA and ^2H electric field gradient tensors are taken into account. Reconsideration of the results of a previous study found that the librational motion, not the vibrational motion, accounts for an asymmetry in the ^1H – ^{13}C dipolar coupling tensor of α -calcium formate at room temperature.
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I. INTRODUCTION

Characterization of small-amplitude motions, such as vibrations and librations, is important to understand the structure and dynamics of molecules in solids. For the past few decades, solid-state nuclear magnetic resonance spectroscopy (SSNMR) has been proven to be an excellent tool for such studies.^{1–7} In SSNMR, information about small-amplitude motions is obtained from the effect the motions have on the nuclear spin interaction tensors. Several studies have shown that small-amplitude motions average several nuclear spin interaction tensors such as the chemical shielding anisotropy (CSA),¹ the heteronuclear dipolar coupling interaction,^{2–4} and the electric field gradient (EFG).⁶

Formate ions are known to undergo both vibrational and librational motions in crystalline solids.^{5,8–14} A previous study attempted to characterize the small amplitude motions of formate ions in crystalline calcium formate.¹⁵ They observed an asymmetry in the formate ion's ^1H – ^{13}C dipolar coupling tensor and it was interpreted by considering the vibrations of the formate ion. However, the study of a similar compound, $\text{Cu}(\text{DCOO})_2\cdot 4\text{D}_2\text{O}$, revealed that formate ions in $\text{Cu}(\text{DCOO})_2\cdot 4\text{D}_2\text{O}$ undergo librational motions about an axis in the plane of the formate ion.⁵ Since librational and

vibrational motions have different effects on nuclear spin interaction tensors, it is important to understand the nature of the motions present in calcium formate and how they affect the nuclear spin interaction tensors measured using SSNMR methods. In this study, we identified the small-amplitude motions present in β -calcium formate and their effects on the nuclear spin interaction tensors. We studied the temperature-dependence of the ^{13}C CSA and the ^2H EFG SSNMR spectra of $\text{Ca}(\text{HCOO})_2$ and $\text{Ca}(\text{DCOO})_2$, respectively. The results provide useful information of small-amplitude motions in rigid crystalline solids.

II. EXPERIMENT

All experiments were performed on a Chemagnetics Infinity 400 MHz solid-state NMR spectrometer operating at a field of 9.4 T with resonance frequencies of 400.14, 100.61, and 61.42 MHz for ^1H , ^{13}C , and ^2H , respectively. All samples consisted of randomly oriented crystalline powders. For the magic angle spinning (MAS) experiments, the samples were packed in a 5 mm zirconia rotor and performed using either a 5 mm Chemagnetics double or triple resonance MAS probe. The typical spinning speed during MAS experiments was 3.5 kHz. For experiments under MAS conditions, a two-pulse phase modulated (TPPM) decoupling sequence¹⁶ was used for decoupling protons during ^{13}C data acquisition.

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All ^{13}C spectra of $\text{Ca}(\text{HCOO})_2$ were obtained using the cross-polarization (CP) sequence with a contact time of 1.5 ms and a recycle delay of 5–60 s. The lower temperature experiments required a longer recycle delay. An rf field strength of 55 kHz was used for CP, and 90 kHz was used to decouple protons during ^{13}C data acquisition. After CP, a 180° pulse was inserted to refocus the ^{13}C magnetization to overcome difficulties due to receiver dead time and the second half of the spin-echo was acquired. For the one-dimensional dipolar-shift experiments,¹⁷ the proton decoupling frequency had an offset of 64 kHz from the water resonance frequency during data acquisition. This established an effective decoupling field at the magic angle.¹⁸ Magic angle rf irradiation of protons suppressed the proton–proton dipolar interactions, while scaling the ^1H – ^{13}C heteronuclear dipole–dipole interaction by 0.58. The resultant one-dimensional spectrum consisted of the ^{13}C CSA and the scaled ^1H – ^{13}C dipolar coupling interactions.¹⁷ This type of spectrum is referred to as a dipolar-shift spectrum in this article. All ^{13}C spectra were referenced externally through adamantane (38.6/29.5 ppm) relative to tetramethylsilane (TMS).

All nonspinning ^2H experiments on $\text{Ca}(\text{DCOO})_2$ were performed on a home-built probe using a quadrupolar echo sequence, 90° – τ – 90° – τ –acq,¹⁹ with a 90° pulse length of $2\ \mu\text{s}$, $\tau=40\ \mu\text{s}$, and a repetition rate of 3 s. The spectra were acquired with 2048 complex data points, with a dwell of $1\ \mu\text{s}$, and zero-filled to 8192 data points. For the ^{13}C MAS experiments on $\text{Ca}(\text{DCOO})_2$, the ^{13}C signal was directly detected with a 90° pulse length of $3.5\ \mu\text{s}$ and a repetition rate of 60s. The ^2H nuclei were not decoupled during the MAS experiments because the MAS spectra showed no signs of ^{13}C – ^2H dipolar coupling.

Simulations of all spectra were carried out using a FORTRAN 77 program or IGOR 3.14 (Wavemetrics, Tigar, Oregon) on a Macintosh computer. The matrix calculations discussed in Sec. IV were accomplished using MAPLE (Waterloo Maple, Inc., Waterloo, Ontario, Canada) on a Unix workstation. The simulations used standard equations¹⁷ and the equality,

$$\sigma_{22\text{C}} = 3\sigma_{\text{isoC}} - \sigma_{11\text{C}} - \sigma_{33\text{C}}, \quad (1)$$

was used because σ_{isoC} was determined with high accuracy and was found to be independent of temperature.

Calcium formate was purchased from Fluka (Milwaukee, Wisconsin). Calcium hydroxide was purchased from Fisher (Pittsburgh, Pennsylvania) and deuterated formic acid (formyl-D, 98%) was purchased from Cambridge Isotope Laboratories (Andover, Massachusetts). All were used without further purification. To make $\text{Ca}(\text{DCOO})_2$, $\text{Ca}(\text{OH})_2$ and DCOOH were mixed in stoichiometric amounts in excess water and the solution was evaporated to dryness. The synthesized calcium formate was in α -form. The α -calcium formate samples were recrystallized from water at 360 K to obtain β -calcium formate. β -calcium formate is stable for days below 400 K in a dry atmosphere. All calcium formate samples contained 1%–2% CuSO_4 to shorten the T_1 relaxation time. The presence of a small amount of paramagnetic

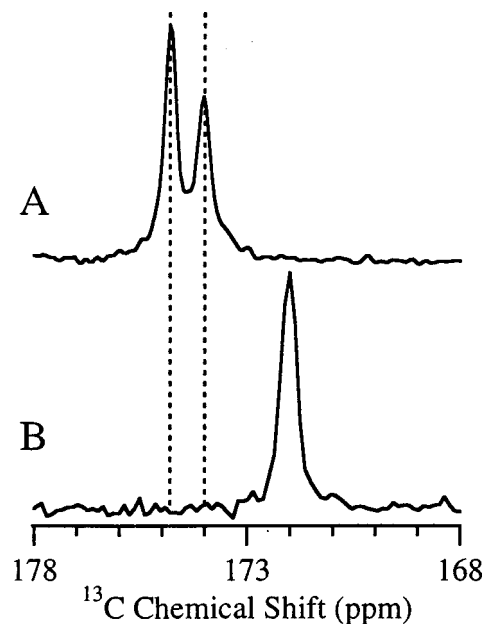


FIG. 1. Carbon-13 CPMAS spectra of (a) a α - $\text{Ca}(\text{HCOO})_2$ powder sample showing two isotropic chemical shift peaks at 174 and 174.8 ppm, and (b) a β - $\text{Ca}(\text{HCOO})_2$ powder sample showing one isotropic chemical shift peak at 172 ppm.

Cu^{2+} ions was found to have a negligible effect on the observed NMR spectra.

III. RESULTS AND DISCUSSION

Several polymorphic species of calcium formate have been reported.²⁰ Two polymorphic species exist at room temperature and they are called α - and β -calcium formate. α -calcium formate is the thermodynamically stable species at room temperature. α -calcium formate has two magnetically different formate ions per asymmetric unit, but there is only one formate ion per asymmetric unit in β -calcium formate.²¹ Figure 1 shows the CP-MAS spectra of these two polymorphs of calcium formate. Figure 1(a) is of an α -calcium formate powder sample, which gives two isotropic ^{13}C chemical shift peaks at 174 and 174.8 ppm, demonstrating the presence of the two formate ions per asymmetric unit. For β -calcium formate powder sample, one isotropic ^{13}C chemical shift peak at 172 ppm was observed, as shown in Fig. 1(b), because there is only one formate ion per asymmetric unit in β -calcium formate. The observed MAS spectrum was identical for both the deuterated and protonated forms of β -calcium formate. A ^{13}C MAS spectrum was obtained before and after each experiment reported here to confirm that the β -calcium formate samples had not converted to α -calcium formate. The isotropic peak of the β -calcium formate samples, $\sigma_{\text{isoC}} = 172.0 \pm 0.1$ ppm, was temperature-independent.

A. Molecular orientation of the tensors

The experimental ^{13}C chemical shift powder pattern of β - $\text{Ca}(\text{HCOO})_2$ obtained at 173 K is shown in Fig. 2(a) (solid line) along with the best-fitting simulated spectrum (dashed line). The root-mean-square deviation (RMSD) was calcu-

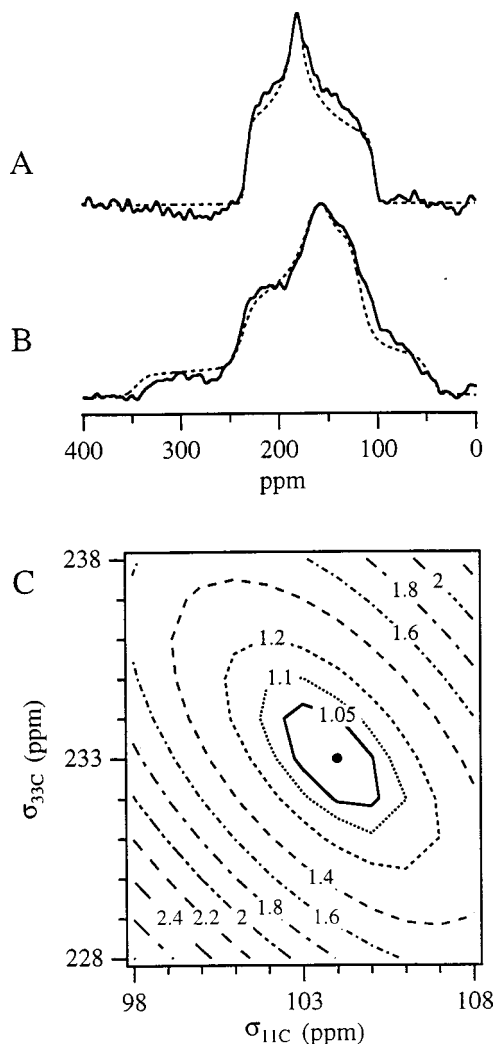


FIG. 2. Carbon-13 chemical shift (a) and dipolar-shift (b) spectra of a β -Ca(HCOO)₂ powder sample obtained at 173 K. The dashed lines are the best-fit simulations. (c) The root-mean-square deviation (RMSD) contour plot relating the simulated ¹³C CSA spectra to the experimental ¹³C CSA experimental spectrum shown in (a). The black dot (●) represents the tensor values of the best-fitting simulation (lowest RMSD) with $\sigma_{11C} = 104$ ppm, $\sigma_{33C} = 233$ ppm, and $\sigma_{330C} = 172$ ppm. The lowest RMSD was normalized to 1, therefore the solid line labeled 1.05 is the 5% error limit.

lated between many simulations and the experimental spectrum in order to estimate the magnitudes of the CSA and their error ranges as explained in a recent publication.²² The best-fitting simulated spectrum had the lowest RMSD between it and the experimental spectrum. Figure 2(c) shows a contour diagram of the calculated RMSD between experimental ¹³C CSA powder pattern obtained at 173 K [Fig. 2(a)] and the simulated spectra. The best-fitting simulation had ¹³C CSA magnitudes of $\sigma_{11C} = 104$ ppm, $\sigma_{22C} = 179$ ppm, and $\sigma_{33C} = 233$ ppm. An identical procedure was used to fit each of the ¹³C CSA spectra reported in this work. The reported errors encompass the 5% error contour line (solid line labeled 1.05 surrounding the best-fitting point).

The ¹³C chemical shift (Fig. 3) and ²H quadrupolar coupling (Fig. 4) powder patterns of β -Ca(HCOO)₂ and β -Ca(DCOO)₂, respectively, showed temperature-dependent averaging of the nuclear spin interaction tensors. In order to

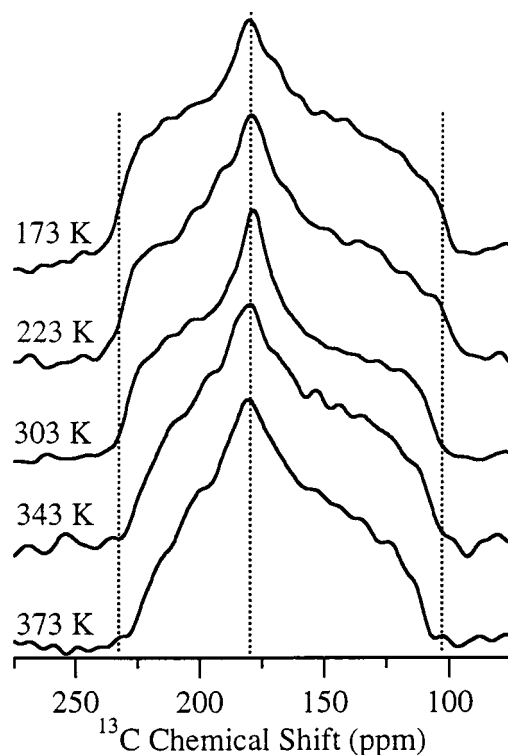


FIG. 3. Carbon-13 chemical shift spectra of a β -Ca(HCOO)₂ powder sample obtained at various temperatures as indicated. Note that the ¹³C chemical shift span decreases with increasing temperature while σ_{22C} is independent of temperature.

correlate the observed spectral averaging with specific molecular motions, the orientation of the ¹³C CSA principal axis system (CSPAS) in the molecular frame of the formate ion was determined using the one-dimensional dipolar-shift method.¹⁷ To determine the orientation of the ¹³C CSPAS in the molecular frame, the dipolar-shift spectrum was obtained at 173 K and is shown in Fig. 2(b) (solid line). The orientation of the ¹³C CSPAS in the molecular frame was determined by simulating the dipolar-shift spectrum using standard equations relating the ¹³C CSPAS to the ¹H-¹³C dipolar

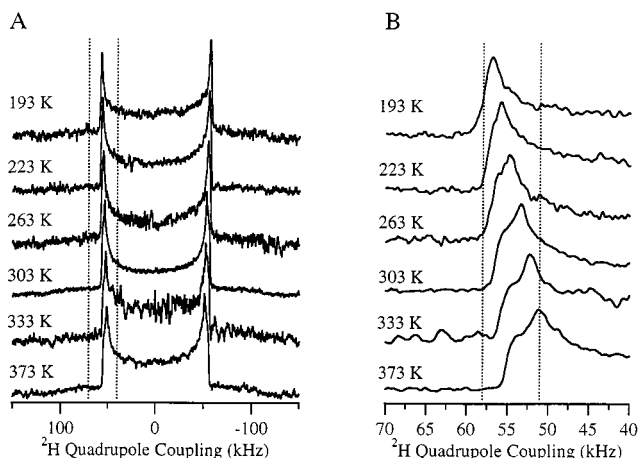


FIG. 4. Deuterium quadrupole coupling spectra of a β -Ca(DCOO)₂ powder sample obtained at various temperatures as indicated: full spectra (A) and the 40–70 kHz region of the full spectra (B).

coupling tensors.¹⁷ Based on the best-fitting simulation [Fig. 2(b), dashed line], the angle between σ_{33C} and the C–H bond was determined to be $0 \pm 5^\circ$. The ^1H – ^{13}C dipolar coupling tensor was assumed to be axially symmetric and collinear with the C–H bond. Since the ^1H – ^{13}C dipolar coupling tensor is collinear with σ_{33C} , the orientations of σ_{11C} and σ_{22C} could not be determined from the dipolar-shift powder pattern. The orientation of the ^{13}C CSA tensor was found to be temperature independent by obtaining dipolar-shift spectra at different temperatures (data not shown). The ^1H – ^{13}C dipolar coupling constant was determined to be 19.6 ± 0.5 kHz, which corresponds to a bond length of 1.15 ± 0.01 Å. This bond length is longer than the 0.99 Å predicted by the x-ray crystal structure²¹ and the average bond length of 1.10 Å found by neutron diffraction of α -calcium formate.²³ These differences are caused by vibrational and librational motions and theoretical treatments of these discrepancies have been undertaken by others.^{2–4}

To estimate the orientation of σ_{11C} and σ_{22C} axes in the molecular frame, the results of a single crystal study of α -calcium formate were used.²⁴ α -calcium formate has two formate ions per asymmetric unit and the orientation of both ^{13}C CSA tensors in the molecular frame were reported. One of these formate ions is symmetric and the other has C–O bond distances differing by 0.02 Å.²³ The C–O bond distances are expected to strongly influence of ^{13}C CSA tensor orientation because both oxygen atoms are directly bonded to the carbon atom. In β -calcium formate, there is only one formate ion per asymmetric unit and it is not symmetrical; its C–O bond distances differ by 0.018 Å,²¹ which is similar to the 0.02 Å difference found for one of the formate ions in α -calcium formate. Therefore, the ^{13}C CSA tensor orientation of β -calcium formate should be similar to the ^{13}C CSA tensor orientation of the nonsymmetric formate ion in α -calcium formate. The single crystal study showed that σ_{22C} is tilted out of the formate ion's molecular plane by 12° . A similar tilt was assumed for σ_{22C} in β -calcium formate.

The orientation of the ^2H EFG tensor in β -Ca(DCOO)₂ has not been determined. However, the orientation of the ^2H EFG tensor was determined for Cu(DCOO)₂·4D₂O by a single crystal study.⁵ Those results showed that V_{zz} is collinear with the C–D bond, V_{xx} is perpendicular to the plane of the formate ion, and V_{yy} is in the plane of the formate ion and perpendicular to V_{zz} and V_{xx} . We assumed that the orientation of the EFG tensor in Ca(DCOO)₂ is close to the orientation found in Cu(DCOO)₂·4D₂O. Figure 5 shows the relative orientation of the ^{13}C CSA and ^2H EFG tensors in the molecular frame, where V_{zz} and σ_{33C} are collinear with the C–D bond which points out of the page. The angle between the V_{yy} and σ_{22C} axes, β , will be discussed later.

B. Root-mean-square amplitudes of vibration

The Wilson **GF** matrix method²⁵ is considered the standard method for treating molecular vibrations. Several excellent books have been written that describe what follows in greater detail and show how to apply it to different molecules.^{25–27} In this section, we will briefly describe the methods and equations used to find the mean-square ampli-

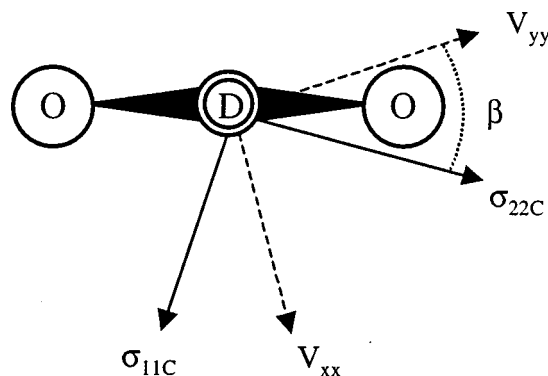


FIG. 5. The orientation of the formate ion with the C–D bond directed along the normal to the page. This shows the relative orientations of the ^{13}C chemical shift (σ_{iiC}) and ^2H electric field gradient (V_{ii}) tensors in the molecular frame. V_{zz} and σ_{33C} are not shown and are assumed to be along the C–D bond. The angle $\beta = 35^\circ$.

tudes of the vibrations of the formate ion. This overview is an abbreviated version of the summary given in Sec. 8.5 of Califano's book.²⁶

The mean-square amplitude of a normal coordinate Q_i in the harmonic approximation is given by

$$\langle Q_i^2 \rangle = \frac{h}{8\pi^2 c \omega_i} \coth\left(\frac{hc\omega_i}{2kT}\right), \quad (2)$$

where k is Boltzmann's constant, T is the temperature in Kelvin, h is Planck's constant, c is the speed of light in cm/s, and ω_i is the harmonic vibrational frequency in cm^{-1} .

The Wilson **GF** matrix method requires a frame transformation from the normal coordinates to the symmetry (or internal) coordinates and use of the approximate expression²⁸

$$\coth x \approx \frac{1}{x} + \frac{x^2}{4}. \quad (3)$$

The mean-square amplitude matrix of the symmetry coordinates becomes

$$\Sigma^s = k\mathbf{T}\mathbf{F}^{-1} + \frac{h^2}{64\pi^2 kT} \mathbf{G}, \quad (4)$$

where \mathbf{F} is the force constant (F) matrix and \mathbf{G} is the G -matrix. For the formate ion, the F -matrix has been reported, but not for calcium formate. The F -matrices for HCOO^- and DCOO^- have been reported for lithium formate; they were determined using infrared spectroscopy.²⁹ Since the vibrational frequencies (and hence the force constants) of calcium formate¹³ and lithium formate²⁹ are similar, we used the F -matrices reported for lithium formate to calculate the mean-square amplitudes. The elements of the G -matrix can be evaluated once the geometry of the molecule is known. The general form of the G -matrix for planar molecules of the form XYZ_2 was previously solved.³⁰ A large number of general G -matrices for different molecular shapes have been catalogued and referenced.²⁷ The bond distances and angles used for the calculation of the G -matrix were $r_{\text{C-D}} = 1.1$ Å, $r_{\text{C-O}} = 1.23$ Å, $\angle\text{O-C-O} = 126.3^\circ$, and $\angle\text{O-C-H} = 116.9^\circ$. These values are the averages of the reported values from an x-ray crystal structure²¹ except that

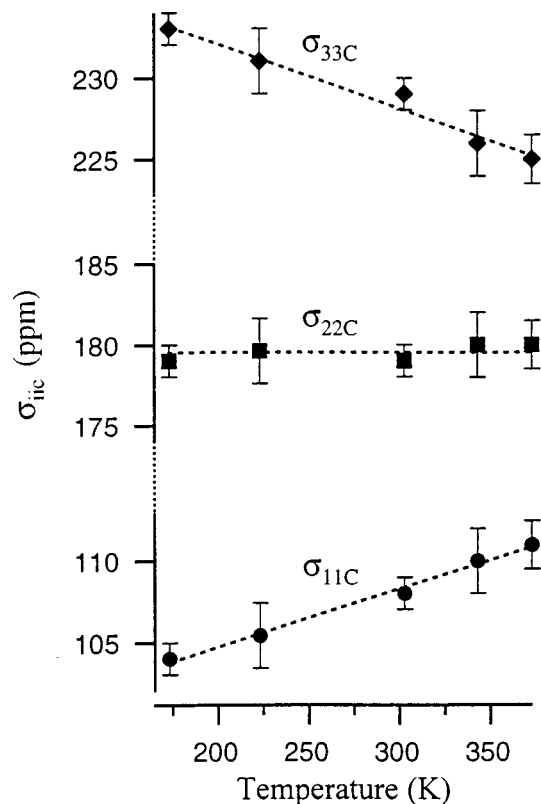


FIG. 6. The temperature-dependence of the magnitudes of the principal elements of the ^{13}C chemical shift tensors of the $\beta\text{-Ca}(\text{HCOO})_2$ powder sample: $\sigma_{11\text{C}}$ (●), $\sigma_{22\text{C}}$ (■), and $\sigma_{33\text{C}}$ (◆) plotted against the absolute temperature with the best-fitting lines (dashed lines).

the C–D bond length is from a neutron diffraction crystal structure reported for α -calcium formate.²³ The results of these calculations found that the root-mean-square amplitudes of the out-of-plane bending mode is $8 \pm 1^\circ$ and the in-plane bending mode is $5 \pm 1^\circ$. It is difficult to estimate the error of the above calculation; however, the listed error was found by varying all of the bond lengths by $\pm 0.2 \text{ \AA}$.

C. Temperature dependence of spectra

Figure 3 shows the ^{13}C CSA powder patterns obtained from $\beta\text{-Ca}(\text{HCOO})_2$ at different temperatures. The width of the observed powder pattern narrowed with increasing temperature. The best-fit CSA tensor values and their errors were determined from RMSD contour plots and are shown in Fig. 6. The magnitudes of $\sigma_{11\text{C}}$ and $\sigma_{33\text{C}}$ changed linearly with temperature. The best-fitting line of the temperature-dependence of $\sigma_{11\text{C}}$ had a slope of $+0.035 \text{ ppm/K}$ and an intercept of 98 ppm . The best-fitting line of $\sigma_{33\text{C}}$ had a slope of -0.040 ppm/K and an intercept of 240 ppm . Unlike $\sigma_{11\text{C}}$ and $\sigma_{33\text{C}}$, $\sigma_{22\text{C}}$ was constant with respect to temperature. The temperature-independent behavior of $\sigma_{22\text{C}}$ and the linearity in the changes of $\sigma_{11\text{C}}$ and $\sigma_{33\text{C}}$ with temperature suggested that a harmonic motion was present in β -calcium formate with its motional axis collinear with the $\sigma_{22\text{C}}$ axis. Both librations and vibrations are harmonic, but the ^{13}C CSA tensor was only expected to be affected by librations because it is located at the center of symmetry of the formate ion.³¹ Here, we modeled the temperature dependence of the ^{13}C

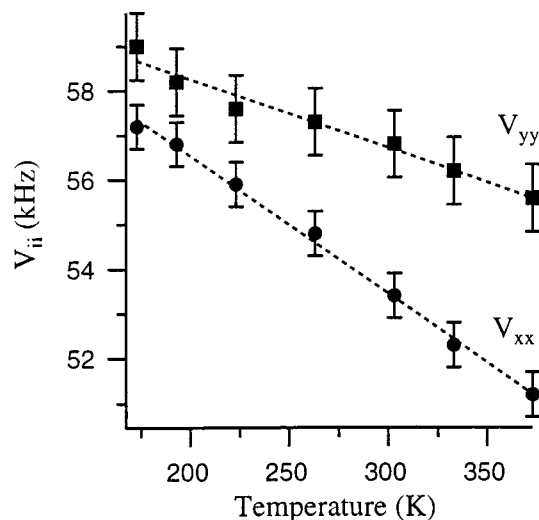


FIG. 7. The observed temperature-dependence of the components of the ^2H electric field gradient tensor of a $\beta\text{-Ca}(\text{DCOO})_2$ powder sample: V_{xx} (●) and V_{yy} (■) plotted against the absolute temperature with the best-fitting lines (dashed lines). The error bars were obtained from the experimental spectra and are ± 500 and $\pm 750 \text{ Hz}$ for V_{xx} and V_{yy} , respectively.

CSA powder patterns as a symmetric libration about $\sigma_{22\text{C}}$. Using established methods,^{6,32} the mean-square amplitude, $\langle \alpha^2 \rangle$, was found to be given by

$$\langle \alpha^2 \rangle = \frac{\sigma_{11\text{C}} - \Sigma_{11\text{C}}}{\Sigma_{33\text{C}} - \Sigma_{11\text{C}}}, \quad (5)$$

where $\Sigma_{11\text{C}}$ is $\sigma_{11\text{C}}$ at absolute zero ($\Sigma_{11\text{C}} = 98 \text{ ppm}$) and $\Sigma_{33\text{C}}$ is $\sigma_{33\text{C}}$ at absolute zero ($\Sigma_{33\text{C}} = 240 \text{ ppm}$). A similar equation was derived to relate the mean-square amplitude to the temperature-dependence of $\sigma_{33\text{C}}$. These equations predicted that

$$\langle \alpha^2 \rangle = (2.6 \pm 0.2) \times 10^{-4} \text{ rad}^2 \text{ K}^{-1} \text{ T}. \quad (6)$$

From this equation, we calculated that the root-mean-square amplitude of the librational motion about $\sigma_{22\text{C}}$ is $12 \pm 1^\circ$ at 173 K and $18 \pm 1^\circ$ at 373 K .

To corroborate the above librational model of the motions in calcium formate, we determined the effects of temperature on the motional averaging of the ^2H EFG tensor using ^2H NMR experiments on a $\beta\text{-Ca}(\text{DCOO})_2$ powder sample. The librational frequencies of the protonated and deuterated formate ions are similar so no effort was made to account for the small mass difference.²⁹ Figure 4(a) shows the full-width ^2H powder patterns and Fig. 4(b) shows the expansion of the 40–70 kHz section of Fig. 4(a). The magnitudes of V_{xx} and V_{yy} decreased with increasing temperature. Figure 7 shows the changes of V_{xx} and V_{yy} vs absolute temperature along with the best-fitting lines (dashed lines in Fig. 7). The best-fitting line of the temperature-dependence of V_{xx} had a slope of -0.031 kHz/K and an intercept of 62.7 kHz . The best-fitting line of the temperature-dependence of V_{yy} had a slope of -0.015 kHz/K and an intercept of 61.3 kHz . The changes in the EFG tensor were linearly correlated with temperature, but the magnitude of change in of V_{yy} was smaller than that of V_{xx} . This suggested that V_{yy} is closer to the motional axis of $\sigma_{22\text{C}}$ than V_{xx} . In order to find the angle

between σ_{22C} and V_{yy}, V_{zz} was assumed to be along the C–D bond.⁵ This made σ_{22C} and V_{yy} in the plane perpendicular to the C–D bond, separated by an angle, β . To find the angle β , equations were derived using standard methods^{6,32} relating the mean-square amplitude of motion about $\sigma_{22C}, \langle \alpha^2 \rangle$, the EFG tensor elements, and the angle β . The resultant equation is given as

$$\sin^2 \beta = \frac{V_{yy} - \Gamma_{yy}}{2\langle \alpha^2 \rangle \Gamma_{yy} + \langle \alpha^2 \rangle \Gamma_{xx}}, \quad (7)$$

where Γ_{yy} is V_{yy} at absolute zero ($\Gamma_{yy} = 61.3$ kHz), Γ_{xx} is V_{xx} at absolute zero ($\Gamma_{xx} = 62.7$ kHz), and $\langle \alpha^2 \rangle$ is the mean-square amplitude determined from the temperature-dependence of the ^{13}C CSA tensor. A similar expression for V_{xx} was derived and both expressions predicted $\beta = 35 \pm 5^\circ$. In our initial attempts to model the temperature-dependence of the ^2H EFG tensor elements, the zero-point vibrations were included as an additional source of motional averaging. However, the best-fitting model did not require zero-point vibrations to be included.

We also attempted to characterize the averaging of the ^1H – ^{13}C dipolar coupling tensor with increasing temperature using the one-dimensional dipolar-shift technique.¹⁷ The dipolar-shift experiments, within experimental error, showed no significant changes with temperature. This was probably due to the poor resolution of the one-dimensional dipolar-shift spectrum. However, we reevaluated the previously reported asymmetry of the ^1H – ^{13}C dipolar coupling tensors of ^{13}C labeled α -calcium formate that was detected by a more sensitive two-dimensional NMR technique.¹⁵ We adopted the reported value of the dipolar coupling, the ^1H – ^{13}C dipolar coupling tensor element orientations, and the notation (D_{xx}, D_{yy}, D_{zz}) used in the previous work. The ^1H – ^{13}C dipolar coupling tensor was assumed to be axially symmetric in the absence of motion. The orientation of D_{zz} was assumed to be along the C–H bond, D_{xx} was perpendicular to the molecular plane, and D_{yy} was in the molecular plane and perpendicular to both D_{xx} and D_{zz} . This assumption made D_{yy} coplanar with σ_{11C} and σ_{22C} and D_{yy} separated from σ_{22C} by 12° . We also assumed the previous ^1H – ^{13}C dipolar coupling experiments were done at 300 K as no temperature was reported. The previous study of the ^1H – ^{13}C dipolar coupling tensor reported motionally averaged magnitudes for the symmetrical formate ion: $D_{xx1} = -10.0$ kHz and $D_{yy1} = -10.9$ kHz. For the nonsymmetrical formate ion, they found $D_{xx2} = -9.2$ kHz and $D_{yy2} = -11.3$ kHz. Zero-point vibrations predicted smaller changes in the ^1H – ^{13}C dipolar coupling tensor than what was observed. The authors suggested that the additional averaging was due to unaccounted librational motions, but they did not consider the problem in detail. Using the librational model proposed in this work, we found that $D_{xx} = -9.0$ kHz and $D_{yy} = -11.4$ kHz. These magnitudes agree well with those found for the nonsymmetrical formate ion in α -calcium formate, which has similar C–O bond lengths to the formate ion in β -calcium formate. Based on this, we conclude that the asymmetry observed in the ^1H – ^{13}C dipolar coupling tensor, which was previously attributed to vibrational motion, is in fact caused by a librational motion similar to the librational motion found in

β -calcium formate described in this work. As with the temperature dependence of the ^2H EFG tensor, the motional averaging of the ^1H – ^{13}C dipolar coupling tensor was completely described by the librational motion.

In this work, a librational motion about σ_{22C} accounted for the temperature-dependent behavior of the spectra of β -calcium formate. The same librational motion accounted for the previously reported asymmetry in the ^1H – ^{13}C dipolar coupling tensor of α -calcium formate. This motion is most likely a combination of the rocking, wagging, and bending librational modes,^{8,12,13} with the wagging mode being the primary motion since it takes place about the molecular axis closest to σ_{22C} . Since vibrational energy levels are large with respect to kT , the librational motion about σ_{22C} plays the dominant role in the temperature-dependent motional averaging of the nuclear spin interaction tensors of calcium formate. No additional averaging of the nuclear spin interaction tensors was observed in the spectra that could be attributed to vibrations.

IV. CONCLUSION

In this article, we studied the temperature-dependent changes of the ^{13}C chemical shift tensor and the ^2H EFG tensor in β -Ca(HCOO)₂ and β -Ca(DCOO)₂, respectively. We used the one-dimensional dipolar-shift spectroscopy technique to determine the orientation of the ^{13}C CSA tensor of β -calcium formate at 173 K so that we could relate the temperature-dependent changes to the molecular motions causing them. We found that the least shielded tensor element, σ_{33C} , is parallel to the C–H bond. We also found the orientation of the ^2H EFG tensor relative to the ^{13}C CSA tensor. Using this orientational information, we demonstrated that the observed temperature-dependence of both of the nuclear spin interaction tensors could be accounted for entirely by a librational motion about the σ_{22C} axis. Even though vibrational motion was also considered, it had no observable effect on any of the data reported here. In light of these results, we reexamined previous work on α -calcium formate that explained an observed asymmetry in the ^1H – ^{13}C dipolar coupling tensor with a zero-point vibrational model and found that the librational model presented here fit the data better than the previously proposed vibrational model.

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