Probing nitrite ion dynamics in NaNO$_2$ crystals by solid-state $^{17}$O NMR

Yizhe Dai$^1$ | Ivan Hung$^2$ | Zhehong Gan$^2$ | Gang Wu$^1$

$^1$Department of Chemistry, Queen’s University, Kingston, ON, Canada  
$^2$National High Magnetic Field Laboratory, Tallahassee, FL, USA

**Abstract**

We report a solid-state $^{17}$O ($I = 5/2$) NMR study of the nitrite ion dynamics in crystalline NaNO$_2$. Variable temperature (VT) $^{17}$O NMR spectra were recorded at 3 magnetic fields, 11.7, 14.1, and 21.1 T. The VT $^{17}$O NMR data suggest that the NO$_2^-$ ion in the ferroelectric phase of NaNO$_2$ undergoes 2-fold flip motion about the crystallographic $b$-axis and the corresponding rotational barrier is $68 \pm 5$ kJ mol$^{-1}$. We also obtained a 2D $^{17}$O EXSY spectrum for a stationary sample of NaNO$_2$ at 250 K, which, in combination with 1D $^{17}$O NMR spectral analyses, allowed precise determination of the relative orientation between the $^{17}$O quadrupolar coupling and chemical shift tensors in the molecular frame of reference. The experimentally determined $^{17}$O NMR tensors for NaNO$_2$ were in agreement with quantum chemical calculations produced by a periodic DFT code BAND.

**KEYWORDS**

molecular motion, oxygen-17, sodium nitrite, solid-state NMR

**INTRODUCTION**

Sodium nitrite, NaNO$_2$, is one of the simplest ferroelectric compounds.$^1$ Below the phase transition temperature, 436 K, the crystal structure of NaNO$_2$ is orthorhombic (space group $Im\bar{2}m$). As shown in Figure 1, the nitrite ion, NO$_2^-$, is in the crystallographic $b$-$c$ plane. The 2-fold symmetry axis of the NO$_2^-$ ion lies along the $b$-direction. Above 436 K, the structure undergoes a transition into a paraelectric phase where the orientation of NO$_2^-$ is disordered with respect to the $b$-axis. These NaNO$_2$ structures have been extensively examined in the past by X-ray diffraction,$^2$-$^5$ neutron diffraction,$^6$-$^7$ $^{14}$N NQR,$^8$-$^9$ and solid-state NMR ($^{23}$Na and $^{15}$N).$^{10}$-$^{12}$ There are also molecular dynamics (MD) simulations on the rotational barriers for NO$_2^-$ motions in solid NaNO$_2$.$^{13}$-$^{14}$ These previous studies have produced overwhelming evidence suggesting that the rotation of NO$_2^-$ about the crystallographic $c$-axis as the mechanism of the NO$_2^-$ polarization reversal in the high-temperature paraelectric phase. However, the actual barrier has never been firmly established by experimental methods. Furthermore, it is interesting to note that, while all previous studies have focused on the NO$_2^-$ rotation about the $c$-axis, little information is known about its rotation about the $b$-axis, which is also the 2-fold molecular symmetry axis. The lack of information about this kind of NO$_2^-$ rotation is not surprising because any NO$_2^-$ rotation/jump about the $b$-axis does not change the electron or nuclear density distributions in the crystal lattice, making all diffraction methods less useful. In addition, solid-state NMR of the naturally abundant magnetic nuclei ($^{23}$Na and $^{14}$N) is also not useful because neither $^{14}$N nor $^{23}$Na NMR parameters are sensitive to the 2-fold jumps of the NO$_2^-$ ion about the $b$-axis. In particular, the 2-fold jump of the NO$_2^-$ ion does change the magnetic shielding and quadrupole interactions at the N atom site. For $^{23}$Na NMR, since the 2-fold jump of the NO$_2^-$ ion does not change the internuclear distance between $^{23}$N and $^{14}$N, the dipolar relaxation mechanism for $^{23}$Na is insensitive to this motion. Our central hypothesis in this study is whether we can utilize the only remaining element in NaNO$_2$, oxygen, to learn about the rotation of NO$_2^-$ about the $b$-axis in solid NaNO$_2$. While solid-state $^{17}$O
(I = 5/2) NMR has become quite common in recent years, to the best of our knowledge, no solid-state $^{17}$O NMR study has been reported for NaNO$_2$. Furthermore, there are few examples in the literature where solid-state $^{17}$O NMR is used to probe molecular motion in solid materials. In this study, our objective is to use solid-state $^{17}$O NMR to probe the NO$_2^-$ ion dynamics in the low-temperature ferroelectric phase of NaNO$_2$. As this study is concerned with the use NMR of a quadrupolar nucleus to probe fundamentally a “chemical exchange” process, we feel that it is particular fitting to report our results in this special issue of the journal honoring Professor Alex Bain, who had a long-term interest in and made important contributions to both areas.

2 | EXPERIMENTAL

$^{[17]}$O]NaNO$_2$ was prepared in the following fashion. To 0.3 mL H$_2$O (40 17O purchased from CortecNet) dissolved 210 mg of NaNO$_2$, followed by addition of a few grains of Amberlite IR120 (acidic form). The solution was left at room temperature for 1 hr. Adding the solution into acetone (5 mL) produced white precipitates, which were collected, washed with acetone (3 × 5 mL), and dried under vacuum (yield: 140 mg $^{[17]}$O]NaNO$_2$). The $^{17}$O enrichment level in $^{[17]}$O]NaNO$_2$ was determined to be 30%. The static $^{17}$O NMR spectra were obtained on Bruker NEO-500 (11.7 T) and Avance-600 (14.1 T) spectrometers. The $90^\circ$ pulse for the $^{17}$O central transition was 4.5 μs. The static $^{17}$O NMR spectra were also recorded at 21.1 T at the NHMFL using a Bruker Avance-III console and a home-built 3.2 mm magic-angle spinning (MAS) probe with the $90^\circ$ pulse for the $^{17}$O central transition being 2.0 μs. A spin-echo sequence was used to obtain undistorted line shapes with the interpulse delay being either 10 or 20 μs. The recycle delays of 50 and 100 ms were used at all temperatures. The static 2D EXSY $^{17}$O spectrum was obtained at 21.1 T with 48 complex $t_1$ increments at 250 K. A mixing time of 1 ms was employed. A liquid H$_2$O sample was used for both RF power calibration and $^{17}$O chemical shift referencing ($\delta = 0$ ppm). Temperature calibrations were carried out either using $^1$H NMR spectra of methanol (11.7 and 14.1 T) or $^{207}$Pb NMR of PbNO$_3$ (21.1 T). Spectral simulations were performed with an in-house MATLAB code.

Quantum chemical calculations of $^{17}$O magnetic shielding and EFG tensors were performed with the periodic DFT code BAND within ADF Modeling Suite 2016. The crystal structure of NaNO$_2$ was used as the starting structures for geometry optimization. The calculations were performed using the TZ2P basis set. The scalar relativistic effects were treated using the zeroth order relativistic approximation (ZORA) formalism. All calculations were performed with kspace = 3 and accuracy = 3 as defined in the BAND program. The computed $^{17}$O magnetic shielding values ($\sigma$) were converted to chemical shifts ($\delta$) by $\delta = 287.5$ ppm − $\sigma$. All quantum chemical calculations were carried out at the Centre for Advanced Computing at Queen’s University (Kingston, ON, Canada) on a Dell PowerEdge R410 Server with 2 sockets with a 6-core Intel Xeon processor (Intel x5675) running at 3.1 GHz.

3 | RESULTS AND DISCUSSION

As a first step of our investigation, it is necessary to determine the $^{17}$O chemical shift (CS) and quadrupolar coupling (QC) tensors and their relative orientation in the molecular frame of NaNO$_2$. To this end, we recorded $^{17}$O NMR spectra for NaNO$_2$ under both MAS and static conditions at the lowest possible temperatures accessible on the probeheads of our spectrometers. Figure 2 shows the $^{17}$O MAS NMR spectrum of $^{[17]}$O]NaNO$_2$ recorded at 205 K and at 21.1 T. The presence of significant intensities across the spinning sideband manifold suggests that the chemical shift anisotropy is large. In addition, the central band is also large. The simulation of the 1D $^{17}$O MAS spectrum yields: $\delta_{iso}(^{17}$O) = ppm, $\sigma(^{17}$O) = 11.05 MHz, and $\eta_Q = 0.58$. To determine the $^{17}$O CS and QC tensor orientations, we recorded the $^{17}$O static NMR spectra of $^{[17]}$O]NaNO$_2$ at 137 K (21.1 T) and 239 K (11.7 T), as also shown in Figure 2. The static spectra also display features that arise from the interplay of magnetic shielding and second-order quadrupole interactions. The static $^{17}$O NMR spectrum obtained at 21.1 T spans a range of about 700 ppm.
applied field strength is an indication that both 17O NMR spectra are of comparable widths (85 and 88 kHz). However, on the frequency scale (in Hz), the 2 17O NMR spectra of [17O]NaNO2 at low temperatures. A, 15-kHz MAS at 21.1 T and 205 K. B, static at 21.1 T at 137 K. C, static at 11.7 T at 239 K.

![FIGURE 2](image)

whereas that obtained at 11.7 T covers more than 1300 ppm. However, on the frequency scale (in Hz), the 2 static spectra are of comparable widths (85 and 88 kHz). This apparent insensitivity of the line width (in Hz) to the applied field strength is an indication that both 17O quadrupolar coupling and chemical shift anisotropy are large for the functional group under study, as we pointed out previously.30,47

These 17O MAS and static NMR spectra can be readily analyzed following a well-established procedure.15,48 By fitting simultaneously the MAS and static spectra, we were able to extract the 17O CS and QC tensor components and their relative orientations. It is also well known that the accuracy of the tensor parameters especially the CS tensor components obtained from such 1D spectral analysis is somewhat limited due to the fact that there are at least 3 adjustable variables (some Euler angles can be fixed due to molecular symmetry). Recently, we showed that an analysis of 2D EXSY spectra allows one to obtain accurate information about the tensor parameters and their relative orientations.30 To further refine the 17O NMR tensor parameters obtained for NaNO2, we obtained a 2D EXSY 17O NMR spectrum for [17O]NaNO2 at 250 K. As seen from Figure 3, the detailed 2D EXSY pattern can be precisely matched by spectral simulation. It is interesting to note that the 2D EXSY pattern shown in Figure 3 is drastically different from that observed for [17O]NaNO3 where the NO3– ion undergoes 3-fold jumps.30 By combining 1D and 2D 17O NMR data, we were able to obtain accurate 17O NMR tensor parameters. The final 17O NMR tensor parameters for solid NaNO2 are reported in Table 1. To obtain an independent confirmation about the 17O NMR tensor orientations in the crystal lattice of NaNO2, we performed quantum chemical calculations using the periodic DFT code BAND.34–40 The computational results are also listed in Table 1. In general, the agreement between experimental and computed results is reasonable, which is in line with the observations seen in previous studies.49

Figure 4 shows the experimentally determined 17O NMR tensor orientations in the molecular frame of NaNO2. For the 17O CS tensor, the δ33 component is perpendicular to the crystallographic b-c plane which contains the planar NO2 ion. This is identical to what has been observed in NaNO3.30 The δ11 component is 138° off the N–O bond. It is interesting that this 17O CS tensor orientation for the NO2– ion is similar to those reported for R–S–N=O40 and nitroxyl (H–N–O).51 This is not totally unexpected because the N–O bond in the NO2– ion does contain a partial double-bond character due to the resonance structures O=N–O ↔ O=N–O. As also seen in Figure 4, the 17O QC tensor seems to be completely determined by the local molecular geometry. That is, χzz and χyy are in-plane and perpendicular and parallel to the N–O bond, respectively. Once again, this 17O QC tensor orientation is identical to that observed for R–S–N=O50 and H–N–O.51 In principal, one can obtain only the relative orientation between the two 17O NMR tensors from experimental data. However, in many cases including the current one, the 17O QC tensor is entirely fixed to the N–O bond (ie, χzz is in-plane and perpendicular to the N–O bond). The 17O QC tensor can be readily linked to the molecular frame of reference.

After obtaining the fundamental 17O NMR tensor information, we are now ready to investigate the NO2– ion dynamics in NaNO2. To this end, we recorded VT 17O static NMR spectra for [17O]NaNO2 at 3 magnetic fields, 11.7, 14.1, and 21.1 T. As seen from Figure 5, the general line shapes are highly dependent on the applied magnetic field, because of the interplay between CS and QC tensors, as mentioned earlier. More importantly, at each magnetic field, as the temperature of the sample increases, the 17O static NMR spectra display drastic changes, reflecting on the chemical exchange process as a result of NO2– jumps. As seen from Figure 4, since the 17O NMR tensors have different orientations in the molecular frame before and
after each 2-fold jump, the 2 symmetry-related oxygen sites would experience different NMR frequencies when the applied magnetic field is along a general direction other than the \( a \)- and \( b \)-axes. The experimentally observed line shapes can be properly modeled by assuming that each \( \text{NO}_2^\cdot \) ion undergoes 2-fold jumps about the molecular symmetry axis, the \( Z_{\text{MF}} \) axis (also the \( b \)-axis) as defined in Figure 4. We also note that at high temperatures such as > 333 K, the simulated spectra display small discrepancies at the low frequency end, showing that the simulated spectra are slightly broader than the observed ones. This must be due to the fact that the unit cell of solid \( \text{NaNO}_2 \) expands with temperature.\(^5\) This assessment is consistent with the fact that both \( ^{14}\text{N} \) NQR\(^6,9\) and \( ^{23}\text{Na} \) NMR\(^10,11\) signals of solid \( \text{NaNO}_2 \) change gradually with temperature. In our model, we assumed that the \( ^{17}\text{O} \) NMR tensor parameters do not change as a function of temperature. It is plausible that this assumption begins to break down as the temperature increases.

The Arrhenius plot generated from all VT \( ^{17}\text{O} \) NMR data is shown in Figure 6, from which the activation energy (\( E_a \)) for the 2-fold jumps of \( \text{NO}_2^\cdot \) in solid \( \text{NaNO}_2 \) was estimated to be 68 ± 5 kJ mol\(^{-1}\). This \( E_a \) value is significantly larger than that determined for the 3-fold jumps of \( \text{NO}_3^- \) in solid \( \text{NaNO}_3 \), 37 kJ mol\(^{-1}\).\(^{30}\) It would be interesting to see whether we can rationalize this difference on the basis of the 2 crystal structures. In \( \text{NaNO}_2 \), each of the 2 oxygen atoms of the \( \text{NO}_2^\cdot \) ion is coordinated to 3 \( \text{Na}^+ \) ions with the \( \text{O}--\text{Na} \) distances being 2.542 Å (1 bond) and 2.462 Å (2 bonds).\(^2-5\) Thus, the 2-fold jump (rotation about the \( b \)-axis) of the \( \text{NO}_2^\cdot \) ion would break a total of

\[Z_{\text{MF}}\]

\[Y_{\text{MF}}\]

\[\chi_{yy}\]

\[\chi_{zz}\]

\[\delta_{11}\]

\[\delta_{22}\]

\[\beta\] degree

\[\gamma\] degree

\[\delta_{11}/\text{ppm}\]

\[\delta_{22}/\text{ppm}\]

\[\delta_{33}/\text{ppm}\]

\[\alpha/\text{degree}\]

\[\beta/\text{degree}\]

\[\gamma/\text{degree}\]

\[\text{C}_{\text{Q}}/\text{MHz}\]

\[\eta_{\text{Q}}\]

\[\delta_{\text{ii}}/\text{ppm}\]

\[\delta_{\text{jj}}/\text{ppm}\]

\[\delta_{\text{22}},/\text{ppm}\]

\[\delta_{\text{33}},/\text{ppm}\]

\[\text{TABLE 1} \]

Experimental and computed \( ^{17}\text{O} \) NMR parameters for \( \text{NaNO}_2 \).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Computation</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{\text{Q}}/\text{MHz} )</td>
<td>12.13</td>
<td>11.05 ± 0.05</td>
</tr>
<tr>
<td>( \eta_{\text{Q}} )</td>
<td>0.51</td>
<td>0.58 ± 0.02</td>
</tr>
<tr>
<td>( \alpha/\text{degree})</td>
<td>(-90^\circ)</td>
<td>(-90 ± 1^\circ)</td>
</tr>
<tr>
<td>( \beta/\text{degree})</td>
<td>(147^\circ)</td>
<td>(149 ± 1^\circ)</td>
</tr>
<tr>
<td>( \gamma/\text{degree})</td>
<td>(-90^\circ)</td>
<td>(-90 ± 1^\circ)</td>
</tr>
<tr>
<td>( \delta_{11}/\text{ppm} )</td>
<td>659</td>
<td>642 ± 2</td>
</tr>
<tr>
<td>( \delta_{22}/\text{ppm} )</td>
<td>1144</td>
<td>1104 ± 10</td>
</tr>
<tr>
<td>( \delta_{33}/\text{ppm} )</td>
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<td>651 ± 10</td>
</tr>
<tr>
<td>( \delta_{22}/\text{ppm} )</td>
<td>132</td>
<td>173 ± 10</td>
</tr>
<tr>
<td>( \alpha/\text{degree})</td>
<td>(-90^\circ)</td>
<td>(-80 ± 1^\circ)</td>
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<tr>
<td>( \beta/\text{degree})</td>
<td>(82^\circ)</td>
<td>(90 ± 1^\circ)</td>
</tr>
<tr>
<td>( \gamma/\text{degree})</td>
<td>(-0.6^\circ)</td>
<td>(0 ± 1^\circ)</td>
</tr>
</tbody>
</table>

\(^*\)The Euler angles are defined with respect to the molecular frame shown in Figure 4.

FIGURE 3 Experimental (black trace) and simulated (red trace) static \( ^{17}\text{O} \) 2D EXSY spectra of \( [^{17}\text{O}]\text{NaNO}_2 \) at \( B_0 = 21.1 \text{ T} \) and \( T = 250 \text{ K} \).

FIGURE 4 Orientations of the \( ^{17}\text{O} \) CS and QC tensors in the molecular frame (MF) of reference for \( \text{NaNO}_2 \). Note that the \( Z_{\text{MF}} \) and \( Y_{\text{MF}} \) are also the crystallographic \( b \) and \( c \) axes, respectively.
six O\textsuperscript{-}–Na\textsuperscript{+} ionic bonds. In NaNO\textsubscript{3}, each of the 3 oxygen atoms of the NO\textsubscript{3}\textsuperscript{-} ion is coordinated to 2Na\textsuperscript{+} ions with the O–Na distance being 2.393 Å.\textsuperscript{52} So the 3-fold jump of the NO\textsubscript{3}\textsuperscript{-} ion needs to break also a total of six O\textsuperscript{-}–Na\textsuperscript{+} ionic bonds. Since the six O\textsuperscript{-}–Na\textsuperscript{+} ionic bonds in NaNO\textsubscript{3} are all shorter (so stronger) than those in NaNO\textsubscript{2}, one would expect that the \( E_a \) value for the NO\textsubscript{3}\textsuperscript{-} 3-fold jumps in NaNO\textsubscript{3} to be higher than that for the NO\textsubscript{2}\textsuperscript{-} 2-fold jumps in NaNO\textsubscript{2}. This is exactly opposite to what we have observed. Closer inspection of the crystal structures reveals that all the O\textsuperscript{-}–Na\textsuperscript{+} ionic bonds in NaNO\textsubscript{3} are roughly perpendicular to the NO\textsubscript{3}\textsuperscript{-} plane. As a result, significant O\textsuperscript{-}–Na\textsuperscript{+} interactions exist in the transition state of the 3-fold jump, thus lowering the \( E_a \) value. On the other hand, only two out six O\textsuperscript{-}–Na\textsuperscript{+} bonds are present in the transition state of the 2-fold jump in solid NaNO\textsubscript{2}. We should point out that the situation of O\textsuperscript{-}–Na\textsuperscript{+} interactions in solid NaNO\textsubscript{3} is very similar to the O···H–N hydrogen bonding environment for the CO\textsubscript{3}\textsuperscript{2}\textsuperscript{-} 3-fold jump within a molecular cage.\textsuperscript{28} In this latter case, the \( E_a \) value for CO\textsubscript{3}\textsuperscript{2}\textsuperscript{-} 3-fold jump is only 22 kJ mol\textsuperscript{-1}.

4 | CONCLUSIONS

We have carried out an extensive solid-state \(^{17}\text{O}\) NMR study to investigate the NO\textsubscript{2}\textsuperscript{-} ion dynamics in the ferroelectric phase of NaNO\textsubscript{2} at 3 magnetic fields. We showed that the NO\textsubscript{2}\textsuperscript{-} ion in NaNO\textsubscript{2} undergoes a 2-fold jump/rotation about the crystallographic \textit{b}-axis with an activation energy of 68 ± 5 kJ mol\textsuperscript{-1}. This is the first time that this type of NO\textsubscript{2}\textsuperscript{-} motion is experimentally probed for NaNO\textsubscript{2}. We demonstrate that solid-state \(^{17}\text{O}\) NMR can offer a unique opportunity to detect molecular motion in solids that are inaccessible by diffraction techniques. It is possible to link the measured motional energetics to molecular interactions such as ionic and hydrogen bonding interactions.

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