

# Extending $^{17}\text{O}$ transverse relaxation measurement to satellite transitions as a direct probe of molecular dynamics in solids

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## ABSTRACT

We report utilization of transverse relaxation rate ( $R_2$ ) of  $^{17}\text{O}$  ( $I = 5/2$ ) satellite transitions (STs) as a probe of molecular dynamics in solids. A simple theoretical model using spectral density functions is proposed to describe the general  $R_2$  behaviors of half-integer quadrupolar nuclei in solids in the presence of molecular motion (or chemical exchange). Experimental  $^{17}\text{O}$   $R_2$  data recorded for both CT and ST from  $^{17}\text{O}$ -labeled  $\text{NaNO}_2$  over a large temperature range are used to verify the theoretical predictions. Our theoretical model is shown to be fully consistent with a full quantum mechanical treatment of the chemical exchange problem involving half-integer quadrupolar nuclei in solids by numerically solving the Liouville-von Neumann equation. The new  $^{17}\text{O}$  ST  $R_2$  method was also applied to study the carboxylate flipping motion in two [ $^{17}\text{O}$ ]carboxylic acid-pyridine adducts in the solid state. The advantages of the ST  $R_2$  approach are discussed. This ST  $R_2$  approach adds a new dimension to the currently available CT-based solid-state NMR techniques for probing molecular motion in solids.

## 1. Introduction

We have recently seen strong interests in using solid-state  $^{17}\text{O}$  NMR to probe molecular dynamics in both organic solids and solid materials [1–23]. This wave of recent studies on molecular motion can be seen as a part of continuing efforts in expanding solid-state  $^{17}\text{O}$  NMR spectroscopy into areas of organic/biological molecules and bio-materials [24–33]. In fact, solid-state  $^{17}\text{O}$  NMR was already proven useful for studying molecular motion in some earlier studies of solid materials [34–38]. So far, probing molecular motion in solids by  $^{17}\text{O}$  NMR methods (or by solid-state NMR for half-integer quadrupolar nuclei in general) has largely relied on detection of the central transition (CT,  $m = +1/2 \leftrightarrow m = -1/2$ ) because this particular single-quantum transition is free of line broadening from the first-order quadrupole interaction,  $Q^{(1)}$  [39]. With the aid of magic-angle spinning (MAS) and in some cases MQMAS [40], reasonably high spectral resolution can be achieved for  $^{17}\text{O}$  at moderate magnetic fields, which can be further improved with the availability of ultrahigh magnetic fields [41].

The CT-based  $^{17}\text{O}$  NMR techniques for studying molecular motion include (1) 1D CT line shape analysis under for static and MAS powder samples, (2) relaxation time measurements ( $T_1$ ,  $T_2$ ,  $T_{1\rho}$ ) for static

powder samples, (3) 2D EXSY experiments (under both MAS and static conditions), and (4) stimulated-echo signal analysis for static powder samples. However, in some cases, due to the presence of multiple sites and a combination of second-order quadrupole and anisotropic magnetic shielding interactions, the observed CT  $^{17}\text{O}$  line shapes are not well defined, making it challenging to obtain precise dynamic information. In other cases, a particular technique may be useful only under certain conditions. For example,  $T_{1\rho}$  measurement is limited only to static samples because MAS can cause further complication for spin-locking of half-integer quadrupolar nuclei [42]. In addition, a proper analysis of the experimental data often requires that all the  $^{17}\text{O}$  NMR tensor parameters be known, a condition that may be difficult to meet beyond well-studied model compounds. In the literature, there are also examples where a combined experimental NMR/computational approach was employed in studying molecular motion in the solid state [16,43,44].

In parallel to the CT-based techniques for studying quadrupolar nuclei, there are also a suite of well-established solid-state NMR techniques that are based on detection of satellite transitions (ST, for example,  $m = 1/2 \leftrightarrow m = 3/2$  or  $m = -1/2 \leftrightarrow m = -3/2$ ). These ST-based techniques include SATRAS [45–47], STMAS [48,49], START-MAS [50], DQ-ST [51], ST-PROSPR [52], etc. Because it is generally

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more difficult to detect STs than CTs, the ST-based methods are not as widely employed as the CT-based methods. However, several workers did point out that STs can also be sensitive to molecular motion in solids on a time scale different from that of CT in solids [35,53–56]. In this work, we use  $^{17}\text{O}$  NMR to demonstrate that transverse relaxation of STs can be used to study molecular motion in solids. We develop a new theoretical model to describe the intrinsic quadrupole transverse relaxation times for CT and STs and the influence of molecular motion on their transverse relaxations. This theoretical model was verified experimentally with extensive  $^{17}\text{O}$  transverse relaxation data from both CT and ST recorded for a model compound,  $^{17}\text{O}$ -labeled  $\text{NaNO}_2$ . Our theoretical model was shown to be consistent with the numerical solutions of the Liouville-von Neumann equation in the Liouville space. We further applied this ST transverse relaxation approach to study the carboxylate flipping motion in two  $^{17}\text{O}$ -labeled carboxylic acid-pyridine adducts containing strong OHN hydrogen bonds.

## 2. Theory

The impact of molecular motion on solid-state NMR spectra of half-integer quadrupolar nuclei has been the focus of several studies in the literature [57–62]. All these previous studies, while employing various theoretical treatments of the quadrupole interaction, were primarily interested in changes of NMR line shapes in the presence of molecular motion. Their theoretical predictions were based exclusively on extensive numerical simulations. In this work, our goal is to develop a simple theoretical model from which dynamic information can be readily extracted from experimental transverse relaxation data collected for both CT and STs without the need of knowing a complete set of NMR tensors involved.

### 2.1. A simple theoretical model

In general, the transverse relaxation rate for a single-quantum transition from  $(I, m)$  state to  $(I, m-1)$  state can be written as [63]:

$$R_2 = (R_2)_{\text{adiab}} + \frac{1}{2} \left( \frac{1}{\tau_m} + \frac{1}{\tau_{m-1}} \right) \quad (1)$$

where  $(R_2)_{\text{adiab}}$  is known as the adiabatic width and the second term is the so-called lifetime broadening ( $\tau_m$  and  $\tau_{m-1}$  are the lifetimes of the initial and final states). The adiabatic width is caused by any modulation of the transition frequency  $\omega_{m,m-1}$  by external perturbation, whereas the lifetime broadening is related to the spin-lattice (longitudinal)  $T_1$ -like process.

Now let us first evaluate the lifetime broadening contribution for a half-integer quadrupolar nucleus in the presence of a strong magnetic field. In the discussion that follows, we use  $^{17}\text{O}$  ( $I = 5/2$ ) as an example, although the theoretical treatment is applicable to any  $I$ . The lifetime for the state with  $(I, m)$  is defined as  $\tau_m$  where  $m = \pm 1/2, \pm 3/2, \pm 5/2$  for  $I = 5/2$ . If the first-order quadrupole interaction,  $Q^{(1)}$ , is the main relaxation mechanism as a result of molecular motion in solids, it can be readily shown that the inverse lifetime ( $1/\tau_m$ ) can be written as [63–65]:

$$\left( \frac{1}{\tau_{\pm 1/2}} \right) = K \left( \frac{16}{25} J_1 + \frac{56}{25} J_2 \right) \quad (2)$$

$$\left( \frac{1}{\tau_{\pm 3/2}} \right) = K \left( \frac{56}{25} J_1 + \frac{36}{25} J_2 \right) \quad (3)$$

$$\left( \frac{1}{\tau_{\pm 5/2}} \right) = K \left( \frac{40}{25} J_1 + \frac{20}{25} J_2 \right) \quad (4)$$

where  $J_1$  and  $J_2$  are the standard spectral density functions. In general, for molecular motion with a correlation time  $\tau_c$ , the standard spectral density functions are defined as:

$$J_n(n\omega_0) = \frac{\tau_c}{1 + (n\omega_0\tau_c)^2} \quad (5)$$

where  $n = 0, 1$ , and  $2$ . The common factor  $K$  in eqs. (2)–(4) has the following expression [65]:

$$K = \frac{3}{160} \langle \omega_Q^2 \rangle \quad (6)$$

where  $\langle \omega_Q^2 \rangle$  refers to the averaged value of the square of the nuclear quadrupole coupling constant ( $\omega_Q = 2\pi C_Q$ ) over discrete molecular jumps in solids.

By combining the results from eqs. (2)–(6) into eq. (1), we can obtain the lifetime broadening contributions for the central transition (CT,  $m = +1/2 \leftrightarrow m = -1/2$ ), the first pair satellite transitions (ST1,  $m = +3/2 \leftrightarrow m = +1/2$  or  $m = -1/2 \leftrightarrow m = -3/2$ ), and the second pair satellite transitions (ST2,  $m = +5/2 \leftrightarrow m = +3/2$  or  $m = -3/2 \leftrightarrow m = -5/2$ ) as:

$$\text{CT} : K \left( \frac{16}{25} J_1 + \frac{56}{25} J_2 \right) \quad (7)$$

$$\text{ST1} : K \left( \frac{36}{25} J_1 + \frac{46}{25} J_2 \right) \quad (8)$$

$$\text{ST2} : K \left( \frac{48}{25} J_1 + \frac{28}{25} J_2 \right) \quad (9)$$

Now we turn our attention to the adiabatic width. In isotropic liquids, the adiabatic width in NMR of half-integer quadrupolar nuclei was extensively discussed in the literature especially in the slow motion regime [26]. In a rigid solid, if there is no substantial molecular motion, the adiabatic width should vanish. However, in the presence of molecular motion in solids such as 2-fold flips or  $C_3$  jumps, the molecular motion/jumps will cause a fluctuation of the transition frequency  $\omega_{m,m-1}$  because this frequency depends on the crystallite orientation. This modulation will give rise to a non-zero adiabatic width. As an example, let us consider a classic two-site chemical exchange problem with the frequency difference between the two sites being  $\Delta\omega_{m,m-1}(t)$ . For the CT,  $\Delta\omega_{1/2,-1/2}$  is determined by the second-order quadrupole frequency shift,  $\Delta\omega_{Q2}$  ( $\Delta\omega_{Q2}$  is on the order of  $\omega_Q^2/\omega_0$  where  $\omega_Q$  is the first-order quadrupole frequency). Under such a circumstance, the adiabatic width can be written as:

$$\langle \Delta\omega_{Q2}^2 \rangle J_1(\Delta\omega_{Q2}) = \langle \Delta\omega_{Q2}^2 \rangle \frac{\tau_c}{1 + (\Delta\omega_{Q2}\tau_c)^2} \quad (10)$$

where  $\langle \omega_{Q2}^2 \rangle$  is the averaged value of the square of the second-order quadrupole frequency shift over molecular motion/jumps in solids. As a result, combining eqs. (7) and (10) into (1) gives us the total transverse relaxation for the CT as

$$(R_2)^{\text{CT}} = \frac{3}{160} \langle \omega_Q^2 \rangle \left[ \frac{16}{25} J_1(\omega_0) + \frac{56}{25} J_2(2\omega_0) \right] + \langle \Delta\omega_{Q2}^2 \rangle J_1(\Delta\omega_{Q2}) \quad (11)$$

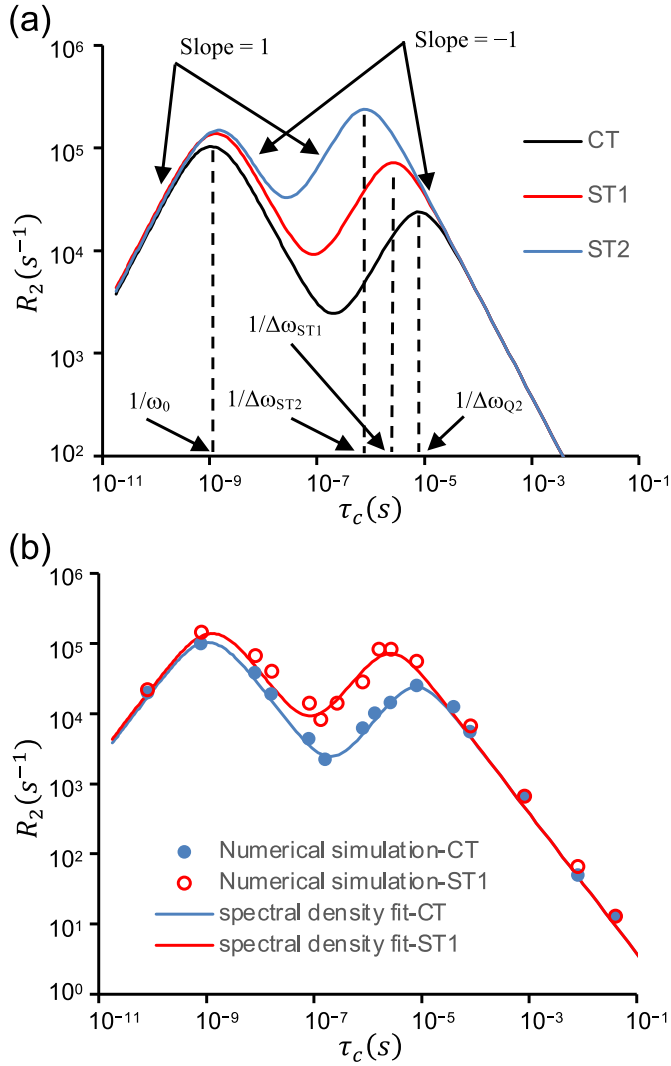
The same argument applies to ST1, except that the ST1 transition frequency contains both the first- and second-order quadrupole frequency shifts. For brevity, we denote the ST1 frequency difference between the two sites as  $\Delta\omega_{\text{ST1}}$ . Then we can write the total transverse relaxation for ST1 as

$$(R_2)^{\text{ST1}} = \frac{3}{160} \langle \omega_Q^2 \rangle \left[ \frac{36}{25} J_1(\omega_0) + \frac{46}{25} J_2(2\omega_0) \right] + \langle \Delta\omega_{\text{ST1}}^2 \rangle J_1(\Delta\omega_{\text{ST1}}) \quad (12)$$

and, similarly, for ST2 as

$$(R_2)^{\text{ST2}} = \frac{3}{160} \langle \omega_Q^2 \rangle \left[ \frac{48}{25} J_1(\omega_0) + \frac{28}{25} J_2(2\omega_0) \right] + \langle \Delta\omega_{\text{ST2}}^2 \rangle J_1(\Delta\omega_{\text{ST2}}) \quad (13)$$

Now with eqs. (11)–(13), we are able to predict how  $R_2$  data would behave for both CT and STs. Fig. 1a shows typical  $R_2$  curves as a function



**Fig. 1.** (A) Illustration of transverse relaxation  $R_2$  curves as a function of molecular correlation time ( $\tau_c$ ) for CT, ST1, and ST2 for  $I = 5/2$ . The parameters used to produce these curves are:  $\omega_0 = 2\pi \times 95 \times 10^6$  (rad/s),  $\omega_Q = 2\pi \times 10 \times 10^6$  (rad/s),  $\Delta\omega_{Q2} = 2\pi \times 20 \times 10^3$  (rad/s),  $\Delta\omega_{ST1} = 2\pi \times 60 \times 10^3$  (rad/s),  $\Delta\omega_{ST2} = 2\pi \times 200 \times 10^3$  (rad/s). (b) Comparison between numerical simulations and spectral density fits with eqs. (11)–(13) where  $\tau_c = (2k_{ex})^{-1}$ .

of molecular correlation time,  $\tau_c$ . Each of the  $R_2$  curves clearly shows two distinct transitions, as first pointed out by Hung et al. [12] for changes in the CT line shape due to chemical exchange. As seen in Fig. 1a, the CT  $R_2$  undergoes the first transition when the molecular motion is comparable with the second-order quadrupole shift,  $\Delta\omega_{Q2}$ , i.e., when  $\tau_c = (\Delta\omega_{Q2})^{-1}$ . As expected, the first transition for the ST1 occurs at a shorter  $\tau_c$  than the transition for the CT. This is because the relevant frequency difference,  $\Delta\omega_{ST1}$ , depends on both the first- and second-order quadrupole interactions and is considerably larger than  $\Delta\omega_{Q2}$ . Thus, the first transition for the ST1 occurs at  $\tau_c = (\Delta\omega_{ST1})^{-1} > (\Delta\omega_{Q2})^{-1}$ . Similarly, the first transition for the ST2 lags further behind occurring at  $\tau_c = (\Delta\omega_{ST2})^{-1}$ , because  $\Delta\omega_{ST2} > \Delta\omega_{ST1} > \Delta\omega_{Q2}$ . After the first transitions, as seen in Fig. 1a, the second transition occurs simultaneously for CT, ST1, and ST2 all at  $\tau_c = (\omega_0)^{-1}$ . Around the second transition, transverse relaxations for CT, ST1, and ST2 are exclusively determined by lifetime broadening.

The most important feature in the  $R_2$  curves shown in Fig. 1a is the fact that all three  $R_2$  curves share exactly the same slope in the slow-motion region (a slope of  $-1$  on a double logarithm scale). It can be readily shown that this slope yields the information about the activation

energy for the molecular jumps once a kinetic model is introduced (*vide infra*). As is clear from Fig. 1a, the benefit of measuring  $R_2$  for all CT, ST1 and ST2 transitions (if possible) is to extend the temperature range for the region with a slope of  $-1$  so that activation energy can be measured with the greatest accuracy. It is also important to note that several other regions also display slopes of  $-1$  or  $1$ . One region is between the two maxima for each  $R_2$  curve and the other is at the fast motion regime. However, one can anticipate some difficulties in utilizing these two regions in practice. For all three transitions, the region between the two maxima spans a rather narrow temperature range making it difficult to allow many data points to be collected. The fast motion region is often prohibited to be accessed either by the practical limitation of high temperatures or sample melting.

To confirm the validity of the spectral density function approach based on eqs. (11)–(13), we employed a full quantum mechanical treatment of the chemical exchange problem involving quadrupolar nuclei in the solid state. As described in a previous study [12], the evolution of a spin system can be generally described in the Liouville space by

$$\frac{d}{dt}\sigma = \widehat{\mathcal{L}}\sigma \quad (14)$$

where  $\sigma$  is the density operator and the Liouvillian  $\widehat{\mathcal{L}}$  includes both the Hamiltonian and relaxation superoperators. For a two-site chemical exchange problem,  $\sigma$  and  $\widehat{\mathcal{L}}$  can be expressed as

$$\sigma = \begin{pmatrix} \sigma_A \\ \sigma_B \end{pmatrix}, \quad \widehat{\mathcal{L}} = \begin{pmatrix} \widehat{\mathcal{L}}_A - k_{ex} \mathbb{I} & k_{ex} \mathbb{I} \\ k_{ex} \mathbb{I} & \widehat{\mathcal{L}}_B - k_{ex} \mathbb{I} \end{pmatrix} \quad (15)$$

where  $k_{ex}$  represents the exchanging rate between sites A and B. All terms of the quadrupolar interaction including those with off-diagonal elements along with the Zeeman Hamiltonian are included in  $\widehat{\mathcal{L}}_A$  and  $\widehat{\mathcal{L}}_B$ . The perturbation from those off-diagonal elements will be automatically taken into account for the high-order quadrupolar shift in the process of solving the equation by finding the eigenvalues of  $\widehat{\mathcal{L}}$ . The imaginary part of the eigenvalues gives rise to oscillations while the real part corresponds to decay of the coherences. For the transverse relaxation calculation, because the oscillatory part is refocused by the spin-echo, only the real part is kept for signal decay of single-quantum coherences (both CT and STs). The selection between CT and STs is controlled by the frequency range set for powder averaging.

Here we used this full quantum mechanical approach to compute  $^{17}\text{O}$   $R_2$  values for both CT and ST1 for a powder sample of  $\text{NaNO}_2$  where the  $180^\circ$ -flipping motion of the nitrite anion was well characterized in the literature [10]. As seen from Fig. 1b, an excellent agreement was found between the numerical simulations and the spectral density fittings based on eqs. (11)–(13). In the numerical simulations, all  $^{17}\text{O}$  NMR tensor parameters reported for solid  $\text{NaNO}_2$  by Dai et al. [10] were used. It is important to point out that, in the positive slope regions ( $10^{-7} < \tau_c < 10^{-5}$  s in Fig. 1b), the numerical simulations suggest that both CT and ST1 display bi-exponential or multi-exponential decays. However, because the fast decaying component for ST1 has exceedingly short  $T_2$  values (ca. 1  $\mu\text{s}$ ), we chose the slow decaying component in the plot. In contrast, the fast decaying component of CT has  $T_2$  values of greater than 50  $\mu\text{s}$ , which can be readily detected experimentally (*vide infra*). Another possible contribution to the non-exponential decays seen in the numerical simulations is a small mixing of the ST1 signal into the CT (or mixing of the ST2 into ST1). Although this kind of signal mixing is expected to be rather small on the basis of their vastly different spectral widths, they may become visible when the mixed signals have very different  $T_2$  values. In practice, one can minimize the possible mixing of ST2 into ST1 by setting the transmitter close to the “horn” position of the ST1 powder pattern, which occurs at  $3C_Q(1 - \eta_Q)/40$  from the isotropic

chemical shift position for  $I = 5/2$  (ignoring the second-order quadrupole shift in ST1). In addition, the non-exponential behavior also introduces uncertainties for the  $T_2$  values used in the theoretical curve shown in Fig. 1b, which appears to exhibit small variations (or “noise”) in the critical region ( $10^{-7} < \tau_c < 10^{-5}$  s). Recently, Vugmeyster et al. [22] applied a similar Liouvillian formalism to treat the nitrate  $C_3$ -jumps in solid  $\text{NaNO}_3$ . Our results shown in Fig. 1b are in agreement with their  $^{17}\text{O}$  CT  $R_2$  and  $R_{1\rho}$  curves.

### 3. Experimental section

The preparation of  $^{17}\text{O}$ -labeled  $\text{NaNO}_2$  was reported previously [10]. Preparation of the adduct of 3,5-dinitro- $^{17}\text{O}_2$ benzoic acid and 3,5-dimethylpyridine was carried out in the following way. 3,5-dinitrobenzoic acid (3,5-DNB, 200 mg, 0.943 mmol) was loaded to a 5 mL pressure tube, to which 140  $\mu\text{L}$   $^{17}\text{O}$ -enriched  $\text{H}_2\text{O}$  (40 %  $^{17}\text{O}$  atom, purchased from CortecNet) was added, followed by addition of 1.5 mL 4 M HCl in dioxane. The mixture was then heated in an oil bath at 110  $^\circ\text{C}$  for 12 h. Upon cooling of the solution to room temperature, most of the solvent was removed with a rotary evaporator until a very viscous liquid was obtained. The viscous liquid was then dissolved in 5 mL acetonitrile and transferred to a 25 mL round bottom flask. 3,5-dimethylpyridine (DMP) (110 mg, 1.03 mmol), which is an oily liquid at room temperature, was added to the flask. The mixture was stirred for 1 h. Evaporating of the acetonitrile with a gentle flow of  $\text{N}_2$  gas led to formation of white solids. The white solids were filtered out and dried under vacuum overnight. 210 mg  $^{17}\text{O}_2$ -3,5-DNB-DMP adduct (0.66 mmol) were obtained. The  $^{17}\text{O}$  enrichment level in the final product was estimated to be 25 % from solution-state  $^{17}\text{O}$  NMR experiment. The pyridinium 2,

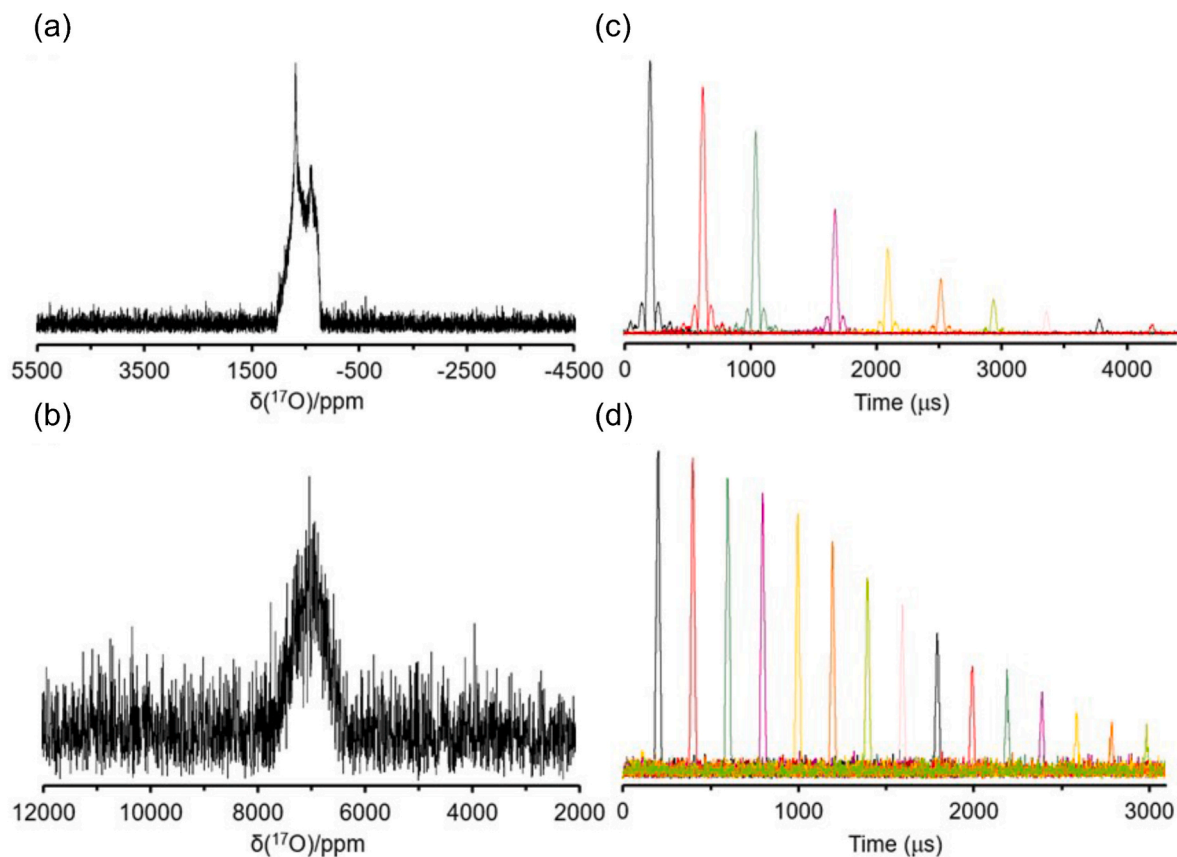
4-dinitro- $^{17}\text{O}_2$ benzoate adduct was prepared in a similar fashion as described above, except that 200 mg 2,4-dinitrobenzoic acid (2,4-DNB) were used and that 100 mg pyridine were added to 2,4-dinitro- $^{17}\text{O}_2$ benzoic acid. The reaction yielded 150 mg pyridinium 2,4-dinitro- $^{17}\text{O}_2$ benzoate as a white solid. The  $^{17}\text{O}$ -enrichment level in the compound was estimated to be 26 % from solution-state  $^{17}\text{O}$  NMR experiment.

$^{17}\text{O}$  transverse relaxation times ( $T_2$ ) were measured using the spin-echo pulse sequence on Bruker Avance-500 (11.7 T) and NEO-700 (16.4 T) NMR spectrometers at different temperatures. Typically, the echo delay was varied between 10 and 200  $\mu\text{s}$ . The  $T_2$  values were determined from the relative echo intensities in time domain. The CT and ST measurements were differentiated by setting the transmitter frequency offset to 500 and 7000 ppm, respectively. Powder sample was packed into a glass tube (5 mm o. d.). The  $^{17}\text{O}$  chemical shifts were referenced to the signal of liquid  $\text{H}_2\text{O}$  at 0 ppm.

### 4. Results and discussion

#### 4.1. $^{17}\text{O}$ -labeled $\text{NaNO}_2$ as a test case

To test the theoretical predictions described in Section 2.1, we recorded  $^{17}\text{O}$   $R_2$  data for both CT and ST1 for a model compound,  $^{17}\text{O}$ -labeled  $\text{NaNO}_2$ . In the crystal lattice of  $\text{NaNO}_2$ , the  $[\text{NO}_2]^-$  anion is known to undergo 2-fold flipping motion and its dynamics was extensively studied [10]. Fig. 2 shows the  $^{17}\text{O}$  CT and ST1 NMR signals from a powder sample of  $^{17}\text{O}$ -labeled  $\text{NaNO}_2$  at 16.4 T. To measure  $R_2$  for CT and ST1, the transmitter was set to 500 and 7000 ppm, respectively. The CT signal displays a characteristic line shape due to a combination of



**Fig. 2.** Experimental  $^{17}\text{O}$  NMR signals for  $^{17}\text{O}$ -labeled  $\text{NaNO}_2$  at 224 K from (a) CT (transmitter set at 500 ppm; echo delay 100  $\mu\text{s}$ ; 2500 transients; recycle delay 0.1 s) and (b) ST1 (transmitter set at 7000 ppm; echo delay 100  $\mu\text{s}$ ; 40000 transients; recycle delay 0.1 s). In (a) and (b), because a whole echo was collected in each case, the signal was shown in the magnitude mode. (c) and (d) are overlays of the spin-echoes collected with different echo delays for CT and ST1, respectively. In (c) and (d), the original FIDs without any manipulation are shown to illustrate the true signal-to-noise ratio.



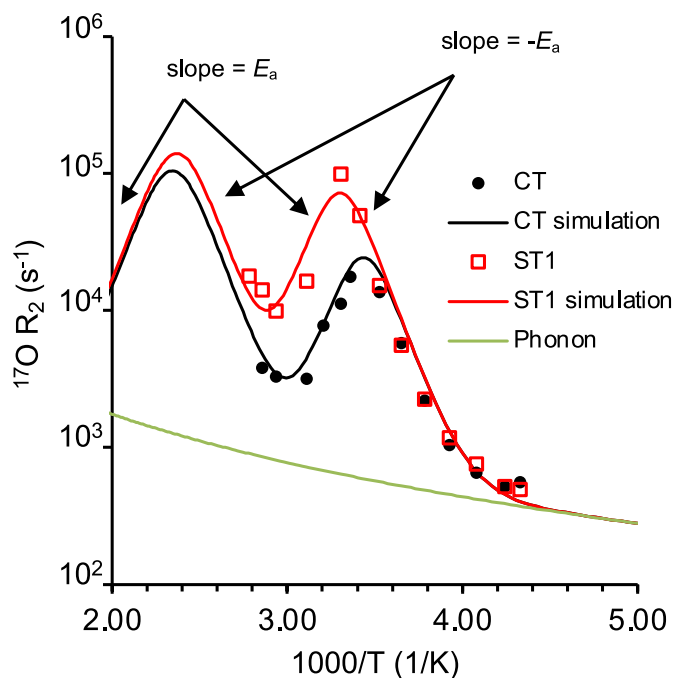
second-order quadrupole interaction and chemical shift anisotropy. But the ST1 signal is just a featureless Gaussian-type line shape, because it represents only a small piece of a very wide ST1 powder line shape. As also seen from Fig. 2, the ST1 signal is considerably weaker than the CT. But in the time domain, both CT and ST1 echoes display excellent signal-to-noise ratios. The  $T_2$  values were determined for both CT and ST1 from the time-domain decays collected with the spin-echo sequence.

Fig. 3 displays all the experimental  $R_2$  data for CT and ST1 and fitting with our theoretical model using eqs. (11)–(13). It should be pointed out that, at a few temperatures around 284 K ( $1000/T \approx 3.5$  in Fig. 3), we observed bi-exponential characteristics in the  $T_2$  decays for CT. In each of these cases, we displayed the shorter  $T_2$  value in Fig. 3. In contrast, all ST1  $T_2$  decays are good exponential decays at all temperatures studied. We will further discuss this issue in the next section. To fit the data shown in Fig. 3 with our theoretical model, we assume the following Arrhenius equation to describe the temperature dependence of  $\tau_c$  (or  $k_{ex}$ ):

$$\tau_c = (2k_{ex})^{-1} = \tau_0 \exp\left(\frac{E_a}{RT}\right) \quad (16)$$

where  $E_a$  is the activation energy for the molecular jumps,  $\tau_0$  is the pre-exponential factor, and  $R$  is the gas constant.

It is well known that, while modulation of electric-field-gradient (EFG) due to large amplitude molecular motions such as the  $180^\circ$  flipping of the nitrite anion in  $\text{Na}_2\text{NO}_2$  is the predominant relaxation mechanism for quadrupolar nuclei in solids, vibrations of apparent rigid atomic lattice known as phonon will also be a relaxation mechanism. For completeness, one should also consider in this work the Raman two-phonon relaxation process (a fluctuation of the first-order quadrupole interaction,  $Q^{(1)}$ , at the nucleus under observation induced by lattice vibration. Thus,  $(R_2)_{\text{phonon}}$  can be considered as the *intrinsic* transverse relaxation in the absence of any chemical exchange. The Raman two-phonon relaxation is known to exhibit a weak temperature dependence in the following fashion [66]:



**Fig. 3.** Comparison between experimental  $^{17}\text{O}$   $R_2$  data (data points) and fitting curves (solid lines) for CT and ST1 obtained for a static powder sample of  $^{17}\text{O}$ -labeled  $\text{NaNO}_2$  at 16.4 T. For the Raman two-phonon process,  $C = 7.0 \times 10^3 \text{ Hz K}^2$ . Other fitting parameters used are:  $\omega_0 = 2\pi \times 95 \times 10^6 \text{ (rad/s)}$ ,  $\omega_Q = 2\pi \times 10 \times 10^6 \text{ (rad/s)}$ ,  $\Delta\omega_{Q2} = 2\pi \times 20 \times 10^3 \text{ (rad/s)}$ , and  $\Delta\omega_{ST1} = 2\pi \times 60 \times 10^3 \text{ (rad/s)}$ .

$$(R_2)_{\text{phonon}} = (R_1)_{\text{phonon}} = CT^2 \quad (17)$$

where  $C$  is a constant related to the averaged amplitude of the  $Q^{(1)}$  interaction in the system. In this work,  $C$  can be treated as a fitting parameter. In general,  $(R_2)_{\text{phonon}}$  is the smallest contribution among all other relaxation mechanisms for quadrupolar nuclei in solids. In some cases where abundant quadrupolar spins are involved, the homonuclear dipolar interaction may be another source of relaxation as part of the intrinsic transverse relaxation. However, in the present study of  $^{17}\text{O}$ , we can safely ignore any homonuclear dipolar contribution.

As seen from Fig. 3, we were able to satisfactorily reproduce the experimental  $R_2$  data for both CT and ST1 using our model, from which we determined that  $E_a = 68 \pm 1 \text{ kJ/mol}$  and  $\tau_0 = 0.5 \times 10^{-17} \text{ s}$ . These values are in excellent agreement with those previously determined from the extensive  $^{17}\text{O}$  line shape analysis for CT spectra of the same compound recorded at four magnetic fields,  $68 \pm 5 \text{ kJ/mol}$  [10,67]. The benefit of the approach demonstrated here is that the fitting of the  $R_2$  curves shown in Fig. 3 does not require any information about  $^{17}\text{O}$  NMR tensors. As also seen in Fig. 3, the activation energy,  $E_a$  is directly reflected on the slopes of the curves. The most important portion of the curve is the slope in the slow-motion regime. In this region, both CT and ST1 data points should partially overlap. Again, the benefit of having ST1 data is that they span a larger temperature range than the CT data, which will make the determination of  $E_a$  more accurate. As a practical matter, one can start the measurement of  $R_2$  for the CT while stepping up the sample temperature until  $R_2$  for the CT reaches its maximal value. Then one switches to measure  $R_2$  for the ST1 at even higher temperatures until the  $R_2$  for ST1 reaches its own maximal value. It is also interesting to note that, in  $\text{NaNO}_2$ , the Raman two-phonon process becomes important at temperatures below 243 K ( $1000/T > 4.0$  in Fig. 3).

It is important to mention that, in this work, we used exclusively the spin-echo sequence to obtain CT and ST1  $R_2$  data. Although we did use the QCPMG sequence to collect some  $T_2$  data for both CT and ST at certain temperatures, we observed significant discrepancies between the two methods. In addition, the  $T_2$  value also appears to depend on the inter-pulse delay used in the QCPMG sequence. Furthermore, in practice it was not possible to use the QCPMG method to measure some very short  $T_2$  values for both CT and ST. Some other issues related to QCPMG were well documented in the literature [68]. For these reasons, we excluded the  $R_2$  data collected by the QCPMG sequence. A detailed study on the difference in quadrupole relaxation  $T_2$  data by the spin-echo and CPMG sequences will appear later.

#### 4.2. Discussion about bi-exponential $T_2$ decays

During the  $T_2$  measurements for CT, we noticed that, at some temperatures especially on the fast side of the Q2 transitions (the intermediate region showing a positive slope), the  $T_2$  decays exhibit significant deviations from a single exponential decay. For ST1, we did not observe this over the temperature range studied. As mentioned earlier, the numerical simulations suggest that the ST1 can exhibit bi-exponential characteristics as well. However, because the fast decaying component of ST1 has very short  $T_2$  values (ca. 1  $\mu\text{s}$ ), it cannot be detected experimentally. In comparison, the fast decaying component of CT has much longer  $T_2$  values ( $>50 \mu\text{s}$ ). The observed non-exponential  $T_2$  decays are fundamentally linked to the  $T_2$  anisotropy often observed in the CT powder spectra (i.e., in the frequency domain). For example, Hoffmann et al. [20] observed significant  $T_2$  anisotropies in the  $^{17}\text{O}$  CT from a powder sample of low-density amorphous ice at 128.9 K. More recently, Vugmeyster et al. [22] also reported observation of non-exponential  $T_2$  decays in  $^{17}\text{O}$  CT NMR for a powder sample of  $\text{NaNO}_3$ . To illustrate this phenomenon, Fig. 4 shows the  $T_2$  decays for CT recorded at 243, 283, and 353 K. Clearly, the  $T_2$  decays at 243 and 353 K are essentially exponential, but that at 283 K shows a prominent bi-exponential character. This phenomenon can be easily understood by considering the

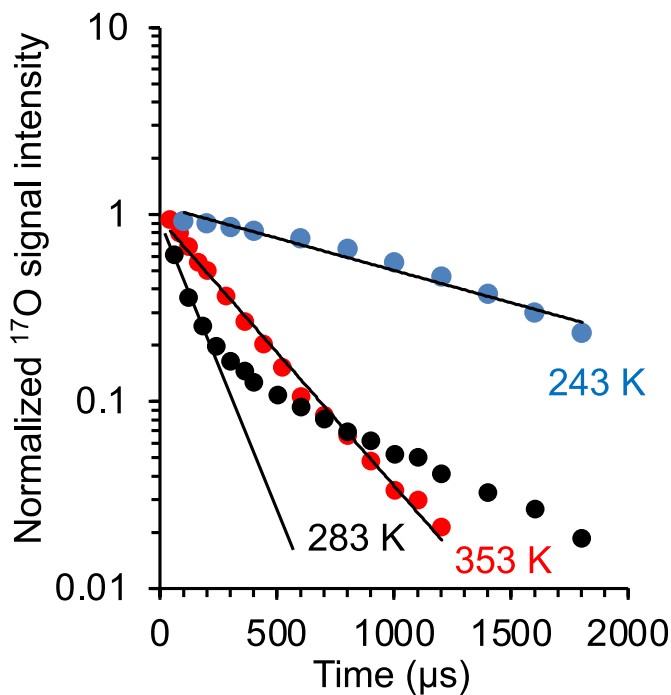


Fig. 4. Comparison of exponential and bi-exponential  $^{17}\text{O}$   $T_2$  decays observed for the CT in  $^{17}\text{O}$ -labeled  $\text{NaNO}_2$  at 16.4 T.

dynamic effect on powder spectra. Let us first examine the exchange broadening at the CT. As is illustrated in Fig. 5, in the  $T_2$  measurement for the CT, one often can excite the whole  $Q^{(2)}$  powder pattern. The molecular reorientation due to motion causes two crystallites to undergo two-site chemical exchange, with the frequency difference between the two signals being on the order of  $\Delta\omega_{Q2}$ . When the motion is slow, all signals experience the same or very similar exchange broadening, which is proportional to  $k_{ex}$ . When the motion increases to become comparable to  $\Delta\omega_{Q2}$  for some crystallites, these crystallites more significant broadening than others, thus giving rise to bi-exponential  $T_2$  decays when all crystallites are observed together. When the motion continues to increase so that  $k_{ex}$  is now greater than  $\Delta\omega_{Q2}$  for all crystallites, the exchange broadenings once again become similar for all crystallites. That is why the bi-exponential or non-exponential  $T_2$  decays are observed only at the intermediate temperatures. The situation for the ST is quite different. As seen in Fig. 5, now the frequency difference between any pair of motion-related crystallites,  $\Delta\omega_{ST1}$ , is much larger than that for the CT. As a result, all crystallites would experience the same exchange broadening for a wide range of  $k_{ex}$ . Even in the fast motion region, all crystallites within the RF excitation profile would still have similar  $T_2$  values.

#### 4.3. Carboxylate flipping in compounds containing OHN hydrogen bonds

After having used the model compound  $\text{NaNO}_2$  to demonstrate the ST  $R_2$  approach, we apply this new method to study the carboxylate flipping motion in two molecular adducts: 3,5-dinitro- $^{17}\text{O}_2$ benzoic acid-3,5-dimethylpyridine adduct (referred to as  $^{17}\text{O}$ -3,5-DNB-DMP in this work) and pyridinium 2,4-dinitro- $^{17}\text{O}_2$ benzoate adduct (denoted as Py- $^{17}\text{O}$ -2,4-DNB in this work). The reason for choosing these two

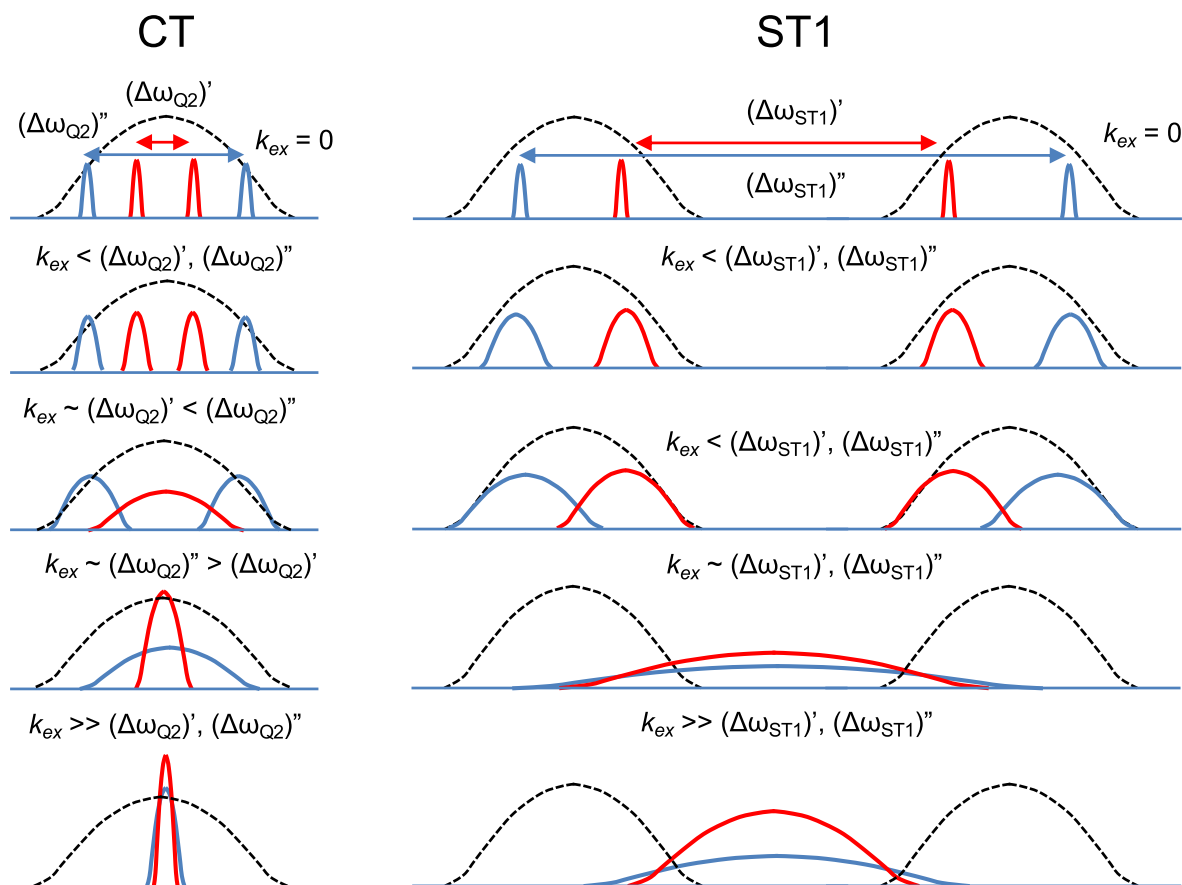
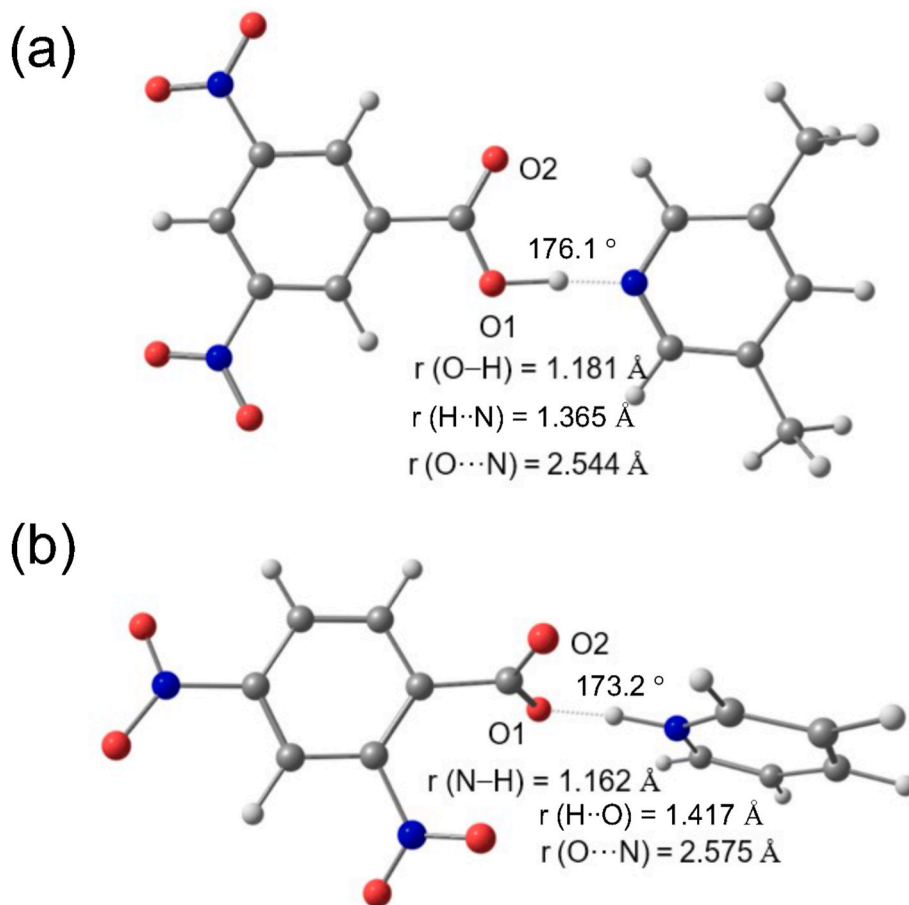


Fig. 5. Illustration of the dynamic effects on signals arising from different crystallites as the origin of the bi-exponential  $T_2$  decays observed mostly for CT in the intermediate exchange regions. The dashed envelope indicates the excitation profile of the RF pulse.



**Fig. 6.** Partial neutron diffraction crystal structures of (a) 3,5-DNB-DMP and (b) Py-2,4-DNB showing the two different types of OHN hydrogen bonds.

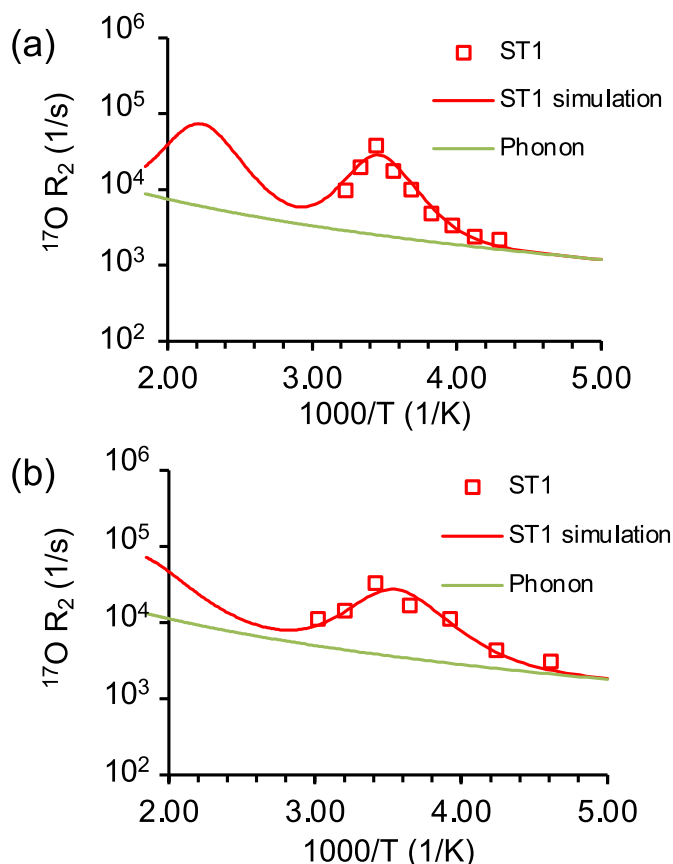
compounds is that they represent two extremes of the very strong OHN hydrogen bonds. As seen in Fig. 6, the neutron diffraction crystal structure of 3,5-DNB-DMP suggests that the central hydrogen atom is closer to the oxygen atom on the carboxylic acid group [69]. So the OHN hydrogen bond in this compound is considered to be of the O–H $\cdots$ N type with the O $\cdots$ N distance being 2.544 Å, which is among the shortest values reported in the literature. In comparison, the central hydrogen atom in Py-2,4-DNB is closer to the nitrogen atom of pyridine, making the hydrogen bond to be of the O $\cdots$ H–N type [70]. It is important to note that the O $\cdots$ N distance in Py-2,4-DNB is also rather short, 2.575 Å. Clearly, on the basis of the neutron diffraction structures, the hydrogen bonds in these two compounds are strong, but exhibit distinct structural features. As previously shown by Lu et al. [13] in the case of nicotinic acid, the carboxylate flipping motion in this kind of OHN hydrogen bonds is fundamentally linked to the hydrogen bond energetics.

To investigate whether the carboxylate flipping motion can reflect the different hydrogen bonding environments in 3,5-DNB-DMP and Py-2,4-DNB, we collected  $^{17}\text{O}$  ST1  $R_2$  data for these two compounds. Fig. 7 shows the experimental results and theoretical fitting. Our analysis yielded the following results: for 3,5-DNB-DMP,  $E_a = 58 \pm 2 \text{ kJ/mol}$  and  $\tau_0 = 2.5 \times 10^{-16} \text{ s}$  and for Py-2,4-DNB,  $E_a = 40 \pm 2 \text{ kJ/mol}$  and  $\tau_0 = 5.0 \times 10^{-13} \text{ s}$ . As also seen in Fig. 7, significant Raman two-phonon contributions were observed in both cases. Interestingly, the static  $^{17}\text{O}$  CT NMR spectra at either 11.7 T or 16.4 T of these two compounds (not shown) do not display enough detailed features which makes a proper line shape analysis rather challenging. Here we were able to obtain dynamic information from the ST  $R_2$  approach without knowing the relevant  $^{17}\text{O}$  NMR tensor parameters. Compared with the result of  $E_a = 48 \text{ kJ/mol}$  reported for nicotinic acid by Lu et al., [13] the corresponding values found for 3,5-DNB-DMP and Py-2,4-DNB are higher and

lower, respectively. The discrepancy can be understood on the basis of the OHN hydrogen bonds formed in the two compounds. As mentioned earlier, the O–H $\cdots$ N hydrogen bond in 3,5-DNB-DMP is strong. In order for the carboxylate group to flip, the hydrogen atom must first migrate to the N end forming an intermediate like O $\cdots$ H–N. This hydrogen migration in 3,5-DNB-DMP costs extra energies. In the case of Py-2,4-DNB, however, the hydrogen atom is already on the N end, i.e., the O $\cdots$ H–N hydrogen bond. Thus, flipping the carboxylate group is easier in Py-2,4-DNB than in 3,5-DNB-DMP.

## 5. Conclusions

We have demonstrated that  $^{17}\text{O}$  ST  $R_2$  data can be used to obtain dynamic information about molecular motion in solids. Our simple theoretical model using spectral density functions clearly shows the two transitions in the transverse relaxation as a response to molecular motion in the solid state. This physical model was shown to be consistent with the numerical simulations by solving the Liouville-von Neumann equation in the Liouville space for the chemical exchange problem involving quadrupolar nuclei. The ST-based approach has the advantage of having a larger “NMR frequency window” than does the CT. Of course, the disadvantage of the ST  $R_2$  method is that the ST generally has weaker signal intensity than the CT. But it is important to point out that, because the ST relaxation measurement is carried out in the time domain, its sensitivity is in fact far superior than that often encountered when working with CT powder line shapes in the frequency domain. In practice, the most efficient way to obtain the activation energy of the motion is to combine CT  $R_2$  and ST  $R_2$  data in the slow-motion region. That is, one can start with the measurement of CT  $R_2$  data until the CT reaches its first transition and then continue to collect ST1  $R_2$  data until



**Fig. 7.** Comparison between experimental  $^{17}\text{O}$   $R_2$  data for ST1 (data points) and fitting curves (solid lines) obtained for static powder samples of (a) 3,5-DNB-DMP and (b) Py-2,4-DNB at 16.4 T. The green line indicates the contribution from the Raman two-phonon process. Other fitting parameters used are: (a):  $\omega_0 = 2\pi \times 95 \times 10^6$  (rad/s),  $\omega_Q = 2\pi \times 7 \times 10^6$ ,  $\Delta\omega_{\text{ST1}} = 2\pi \times 22 \times 10^3$  (rad/s),  $C = 3.0 \times 10^4$  Hz K<sup>2</sup>; (b):  $\omega_0 = 2\pi \times 95 \times 10^6$  (rad/s),  $\omega_Q = 2\pi \times 7 \times 10^6$  (rad/s),  $\Delta\omega_{\text{ST1}} = 2\pi \times 20 \times 10^3$  (rad/s),  $C = 4.5 \times 10^4$  Hz K<sup>2</sup>.

the ST1 also reaches its own first transition. This will ensure the largest temperature span accessible, from which the most accurate determination of activation energy can be achieved. Very often, one is limited by the shortest  $T_2$  value that can be experimentally determined with the currently available technology (ca. a few  $\mu\text{s}$ ). Finally, it should be emphasized that, while this study is concerned with solid-state  $^{17}\text{O}$  NMR for static samples, the strategy demonstrated here is certainly applicable to all other half-integer quadrupolar nuclei under both static and MAS conditions.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Data availability

Data will be made available on request.

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