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A combined ^{17}O RAPT and MQ-MAS NMR study of L-leucine

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Abstract

We report the application of rotor-assisted population transfer (RAPT) to measure the quadrupolar coupling constant (C_q) for spin $\frac{5}{2}$ nuclei. Results from numerical simulations are presented on the magnitude of enhancement factor as a function of frequency offsets, i.e. the RAPT profile. Experimental ^{17}O RAPT profile is traced for the amino acid L-leucine. In addition, results from MQ-MAS experiments are incorporated to determine the quadrupolar asymmetry parameter (η_q). Unlike previous reports, the ^{17}O NMR parameters for an amino acid, L-leucine, is reported at a relatively low field of 9.4 T.

Keywords: Amino acids; ^{17}O; RAPT; MQ-MAS

1. Introduction

Oxygen-17, which is a spin $\frac{5}{2}$ nucleus, has never been as successful as a probe of structure in organic molecules as spin $\frac{1}{2}$ nuclei such as ^{13}C NMR. The combination of a low natural abundance (0.037%), and the large quadrupolar couplings of oxygen in organic molecules have made the ^{17}O NMR measurement a daunting task. There have been a number of renewed efforts in the study ^{17}O NMR of small organic molecules of biological interest in the solid state. This stems from the advent of high-magnetic field strengths ($\geqslant$ 500 MHz ^{1}H frequency), fast spinning rotors and resolution enhancement techniques such as multiple-quantum magic-angle spinning (MQ-MAS) [1]. These recent reports vary from amino acids (alanine, L-glutamic acid), nucleosides (thymine and uracil), monosodium glutamate, polyglycines and polyalanines [2–5]. The magnitude of nuclear quadrupolar coupling constants are typically large, on order of 7–8 MHz. Carbonyl groups located in the α-helix and β-sheet have been distinguished in polypeptides [2,3], and five distinct oxygen environments have been identified in monosodium glutamate [5]. Small differences in the quadrupolar coupling constants have been attributed to the differences in the H-bonding strengths in alanine and in polypeptides. Recently, Dupree and co-workers have compiled ^{17}O NMR parameters for a series of amino acid salts [6] and a transmembrane peptide [7]. Also, a theoretical study has been made to correlate the ^{17}O shielding parameters to hydrogen bonding distances in glutamic acid polymorphs [8].

Here we report NMR data on the amino acid L-leucine. By combining the increased sensitivity of rotor-assisted population transfer (RAPT) [9–11] with high-speed MAS (20 kHz) we can obtain high-quality spectra and extract the NMR parameters at a relatively lower magnetic field (400 MHz ^{1}H frequency) than used in the previous studies.

2. Materials and methods

L-leucine was synthesized by acid catalyzed exchange of oxygen in ^{17}O labelled water at 80 °C. The resulting solution was neutralized with aniline to precipitate the free amino acid [12]. The purity of the sample was determined by powder X-ray diffraction and ^{13}C MAS NMR measurements. All NMR measurements were made on a Bruker Avance 400 MHz spectrometer using 2.5 mm MAS probehead and spinning rates of 20 kHz. One-dimensional

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^{17}O MAS spectra were measured using the sensitivity enhancement scheme RAPT; to obtain the RAPT sensitivity enhancement, frequency switched Gaussian pulses ($\sigma = 2.855\,\mu s$, $\tau_p = 16\,\mu s$; 20 pulse pairs) were applied at pre-determined frequency offsets [9–11]. A 2 μs delay between each pulse in the RAPT pulse train was used to allow time for the transmitter phase to stabilize. A radiofrequency field strength of 35 kHz was used for the RAPT pulse train and a recycle delay of 500 ms. The RAPT-enhanced MAS spectra were acquired with 8192 scans using a RAPT frequency offset of ±500 kHz, 256 scans were acquired to trace the RAPT profile with varying frequency offsets. Shifted-echo method [13,14] was used for acquiring and processing triple quantum MQ-MAS data [15]. A radiofrequency field strength of 72 kHz was used for the excitation and the FAM conversion pulses [16], and 22 kHz for the π pulse. $64t_1$ points (9600 scans) were acquired with an increment of 24 μs at a recycle delay of 100 ms. T_1 measured using saturation recovery method was 25 ms. Tap water (0.0 ppm) was used to calibrate the radiofrequency field and as chemical shift reference.

2.1. Simulations

For simulating the RAPT enhancement profiles we have employed numerical density matrix simulations of a polycrystalline sample containing spin I nuclei to calculate the evolution of an initial density operator $\boldsymbol{\rho}_0$ in the rotating frame according to

$$\boldsymbol{\rho}(\Omega, t) = \mathbf{U}(\Omega, t, 0\boldsymbol{\rho}_0\mathbf{U}^{\dagger}(\Omega, t, 0), \tag{1}$$

where

$$\mathbf{U}(\Omega, t, 0) = \mathbf{T}\,\exp\left\{-i\hbar\int_0^t \mathbf{H}(\Omega, s)\,ds\right\} \tag{2}$$

and $\mathbf{T}$ is the time ordering operator. The time-dependent Hamiltonian in a frame rotating at the transmitter frequency is

$$\mathbf{H}(\Omega, t) = \mathbf{H}_q(\Omega, t) + \hbar\omega_1(t)[\mathbf{I}_x\cos\phi(t) + \mathbf{I}_y\sin\phi(t)] + \hbar\Delta\omega\mathbf{I}_z, \tag{3}$$

where $\mathbf{H}_q(\Omega, t)$ contains the first- and second-order quadrupolar Hamiltonians given by [17]

$$\mathbf{H}_q^{(1)}(\Omega, t)/\hbar = \omega_q A_{2,0}(\Omega, t)\mathbf{T}_{2,0} \tag{4}$$

and

$$\mathbf{H}_q^{(2)}(\Omega, t)/\hbar = -\frac{\omega_q^2}{\omega_0}\sum_{k=1,2}\frac{A_{2,k}(\Omega, t)A_{2,-k}(\Omega, t)[\mathbf{T}_{2,k}, \mathbf{T}_{2,-k}]}{k}. \tag{5}$$

Here $\Omega = (\alpha, \beta, \gamma)$ is a set of Euler angles describing the orientation of the principal axis system of the electric field gradient with respect to the rotor axis system. In all simulations, we will follow the evolution of the powder average of the fictitious spin half [18,19] observables according to

$$\langle\mathbf{I}_\alpha^{r-s}(t)\rangle = \int \mathrm{Tr}\,\boldsymbol{\rho}(\Omega, t)\mathbf{I}_\alpha^{r-s}\}\,d\alpha\,\sin\beta\,d\beta\,d\gamma. \tag{6}$$

For the simulations in this investigation, we typically start with $\boldsymbol{\rho}_0 = \mathbf{I}_z$ and observe $\mathbf{I}_z^{r-s}$.

When dealing with a time-dependent Hamiltonian we adopt the conventional numerical approximation of discretizing the time-dependence into small time-independent periods, and write the propagator matrix in Eq. (2) as

$$\mathbf{U}(\Omega, t, 0) = \prod_n \mathbf{U}(\Omega, n\Delta t, n\Delta t - \Delta t),$$

where

$$\mathbf{U}(\Omega, n\Delta t, n\Delta t - \Delta t) = \exp\{-i\hbar\mathbf{H}(\Omega, n\Delta t)\Delta t\}$$

and the Hamiltonian is assumed to be time independent during the time interval Δt. In this approximation $1/\Delta t$ needs to much larger than the highest frequency in a Fourier expansion of the time-dependent rotating frame Hamiltonian.

3. Results and discussion

For odd-half-integer quadrupolar nuclei such as ^{17}O, the observed total frequency shifts in the MAS spectra (δ_{iso}^{Total}) are directly related to the isotropic chemical shifts (δ_{iso}^{CS}) and isotropic second-order quadrupolar shifts (δ_{iso}^{2Q}) by

$$\delta_{iso}^{Total} = \delta_{iso}^{CS} + \delta_{iso}^{2Q} \tag{7}$$

The second-order isotropic shift is a function of the quadrupolar product (P_q), the Larmor frequency (ν_L) and the spin quantum number (I).

$$\delta_{iso}^{2Q} = \frac{-3[I(I+1) - 3/4]}{40\nu_L^2 I^2(2I-1)^2}P_q^2 \times 10^6, \tag{8}$$

where the quadrupolar product (P_q) is related to the quadrupolar coupling constant (C_q), which in turn is related to the quadrupolar frequency (ν_q) as

$$P_q = C_q\sqrt{1 + \frac{\eta_q^2}{3}}, \tag{9}$$

$$C_q = \frac{e^2qQ}{h}, \tag{10}$$

$$\nu_q = \frac{3C_q}{2I(2I-1)}. \tag{11}$$

Sensitivity enhancement schemes are particularly useful in the study of low natural abundant ^{17}O isotope. The method of RAPT enhances the central transition signal intensity by the saturation of the satellite transitions [20]. The method has been applied to higher spin systems [21] and exploited to enhance the signal intensity in the RIACT-MQ-MAS experiment [22–24]. The enhanced RAPT sequence consists of a train of Gaussian pulses with alternating off-resonant frequencies of $\pm\nu_{off}$ [9–11].

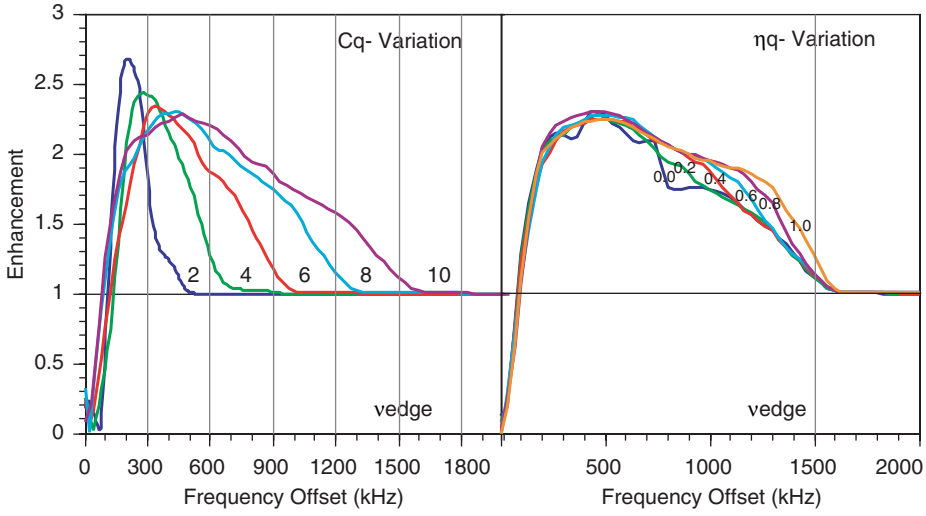

Fig. 1. (a) Simulated RAPT profiles for spin $\frac{5}{2}$ nucleus with C_q values as indicated, η_q was kept constant at 0.2. (b) Simulated RAPT profiles with η_q values as indicated, C_q was kept constant at 10 MHz. Numerical density matrix simulations were performed using 3722 crystal orientations on ^{27}Al nucleus. An radiofrequency power of 35 kHz was used for the Gaussian pulses.

This approach overcomes the need for fast phase shifting and allows to explore a wider range of frequency offsets. The use of Gaussian pulses also improves the selectivity of satellite excitation [9–11]. In Fig. 1a is a plot of the RAPT sensitivity enhancement factor as a function of $|\nu_{\text{off}}|$ for a ^{27}Al nucleus (spin $\frac{5}{2}$) experiencing different C_q values. Enhancements increase to a maximum near $|\nu_{\text{off}}| \approx |3C_q|/40$ and return to unity (no enhancement) when $|\nu_{\text{off}}| \geqslant |3C_q|/20$. Fig. 1b illustrates the dependence of the RAPT sensitivity enhancement on η_q for a fixed C_q value of 10 MHz. With increasing η_q the RAPT enhancement profile becomes broader and returns to unity when $|\nu_{\text{off}}| \geqslant |3C_q|/20$, independent of η_q.This is a consequence of the outermost discontinuity (edge) of the first-order quadrupolar line shape for a satellite transition depending only on C_q. Thus, measurement of the RAPT profile edge frequency, given by $\nu_{\text{edge}} = |3C_q/(2I(2I-1))|$, where I is the spin of the nucleus, provides a simple means for determining C_q. Additionally, the RAPT enhancement profile can provide information on η_q, with steeper RAPT enhancement edges corresponding to higher η_q values. Since the ν_Q is scaled by the spin of the nucleus, C_q values of the order of 3 MHz or greater can be determined easily. However, it is cautioned that with lower C_q values of the order of 2 MHz, it is recommended to use lower power that would not perturb the $\pm\frac{5}{2}$ to $\pm\frac{3}{2}$ transitions thus affecting the ν_{edge} measurements (Fig. 1a). For relatively small couplings (up to 3 MHz), satellite transition are easily excited and are determined by satellite transition NMR [25].

There are 19 coded α-amino acids [R–CH(NH_3^+)–COO^-]. The simplest amino acid, glycine, has no side chain. Next, there are 4 with saturated aliphatic side chains (R = –CH_3 for alanine, –CH_2–CH–$(CH_3)_2$ for leucine, –CH–$(CH_3)_2$ for valine, and (*S*)–CH–(CH_3)–C_2H_5 for iso leucine). Additionally, there are 10 with functionalized side chains and 4 with aromatic or heteroatomic side chains. Proline is a coded α-imino acid [26]. There are only a few reports of ^{17}O NMR spectroscopic investigations examining amino acids containing saturated aliphatic side chains. Gann et al. [12] used multi-field DAS NMR study to distinguish two resonances and estimate the quadrupolar coupling product P_q ($P_q = C_q\,(1+\eta_q^2/3)^{1/2}$, where C_q is the quadrupolar coupling constant in MHz and η_q the asymmetry parameter) in L-alanine. More recently, Wu et al. [4] analyzed the MQ-MAS spectrum and used fitting of MAS spectral line shapes to estimate C_q and η_q of D-alanine, and Pike et al. studied L-alanine [6]. The isotropic shifts are in the range of 260–280 ppm (see Table 1). Four different oxygen environments have been identified in L-glutamic acid HCl [5], an amino acid that contains two carboxylic acid groups. The C_q's are in range of 7.5–8.3 MHz, and the isotropic shifts are 180 ppm for two oxygens and 320 for the other two oxygens. By a combination of double rotation and MQ-MAS, five different oxygen sites have been distinguished in monosodium glutamate (MSG) [5]. The C_q's are in range of 7.5–8.1 MHz, and the isotropic shifts in the range of 250–300 ppm.

The RAPT-enhanced ^{17}O MAS NMR spectrum of L-leucine shows a broad resonance centered at 200 ppm. Fig. 2 and 3 (top). The apparent lack of line shape can be attributed to the slow-to-intermediate range motion [27].

As the results from numerical simulations indicate, in addition to enhancing the sensitivity, the method of RAPT is a viable tool to determine the C_q. This is unlike the MQ-MAS methods where the quadrupolar product P_q is usually determined. By plotting the enhancement factor as a function of offset frequencies (i.e. the RAPT profile), the outer edge (the offset frequency where there is no apparent enhancement), the ν_{edge} can be measured and the quadrupolar coupling constant can be determined [9]. The

Table 1
^{17}O isotropic chemical shift, δ_{iso}, quadrupolar coupling constant, C_q, and quadrupolar asymmetry parameter, η_q, for amino acids that contain saturated aliphatic sidechains

Sites	δ_{iso} (ppm)	C_q (MHz)	η_q	Reference
L-leucine (O1)	256±5	6.3±0.05	0.3±0.05	This work
L-leucine (O2)	285±5	6.93±0.03	0.8±0.05	
L-alanine (O2)	260.5	6.53	0.7	[6]
L-alanine (O1)	284	7.86	0.28	
D-alanine (O2)	262	6.4	0.6	[4]
D-alanine (O1)	275	7.6	0.65	

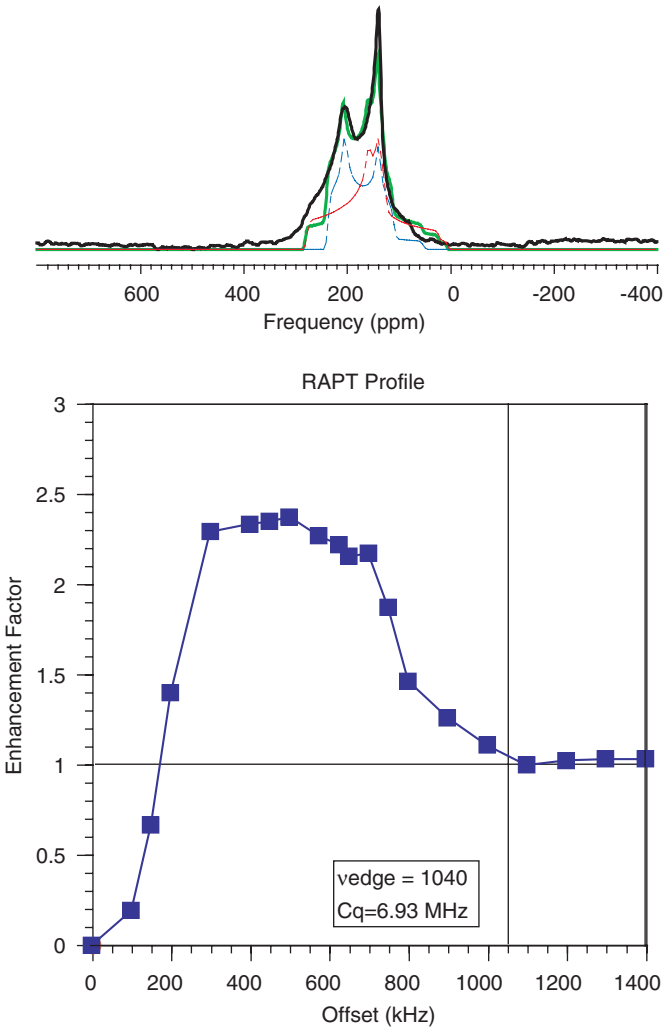

Fig. 2. ^{17}O RAPT-enhanced MAS NMR spectrum of L-leucine (top). The gray line is simulation using the parameters reported in Table 1. The RAPT-enhancement (central transition) as a function of offset frequency (bottom). The vertical line indicates the ν_{edge}.

measured ^{17}O RAPT profile of L-leucine shows enhancement factor 2.4 at an offset frequency of 350 kHz, Fig. 2 (bottom). The enhancement factor drops to 1 near 1100 kHz with a ν_{edge} of 1040±5 kHz. From the equation $\nu_{edge} = |3C_q/(2I(2I-1))|$, the C_q is determined to be 6.93±0.03 MHz. It may be noted that the ν_{edge} is actually a measure of C_q value for the oxygen site having larger quadrupolar interaction.

Isotropic spectra of quadrupolar nuclei are obtained by MQ-MAS using conventional MAS probes [15]. MQ-MAS averages the second order quadrupolar effect to obtain narrow resonances in the isotropic dimension after the shearing transformation to obtain quadrupolar parameters and the isotropic shifts. Mostly, the values derived from the MQ-MAS measurements have been used as a constraint to fit the MAS spectra to simulated line shapes [4,5]. The quadrupolar coupling product (P_q), is obtained by the analysis of the MQ-MAS data, while the quadrupolar coupling constant (C_q) is obtained by the RAPT method. The η_q values are obtained by substituting the C_q values determined from the RAPT experiments. The ^{17}O MQ-MAS spectrum of L-leucine shows two resonances indicating two different oxygen environments. From the position of the resonances in the MAS and the isotropic dimensions, the quadrupolar product (P_q) and isotropic shifts (δ_{iso}) are calculated. Also, the results from the RAPT and MQ-MAS measurements were used as a guideline to fit the RAPT-enhanced MAS spectrum to determine the NMR parameters listed in Table 1. Results from the previous measurements on alanine are also tabulated.

L-leucine crystallizes in monoclinic space group with alternating hydrophilic and hydrophobic layers and form very thin flakes. Due to the low quality of the crystals, the X-ray crystal structures have been recently redetermined at 120 K [28]. The asymmetric unit cell contains two crystallographically independent molecules. For L-leucine the distances are 1.258/1.263 Å and 1.255/1.252 Å for C–O(1) and C–O(2), respectively. In L-alanine the carbon–oxygen bond lengths are 1.242 and 1.258 Å [29]. Wu et al. [4] and Pike et al. [6] contemplate that in L-alanine the stronger H-bonding results in lengthening of the carbon–oxygen bond. Moreover, this strengthening of H-bonding results in the decrease of electric field gradient at the oxygen. The NMR parameters for L-leucine closely resemble that of L-alanine except for the η_q values (Table 1); the O(1) site having a smaller quadrupolar coupling constant. Further studies such as ^{17}O–^{13}C distance measurements by NMR method may be useful [30].

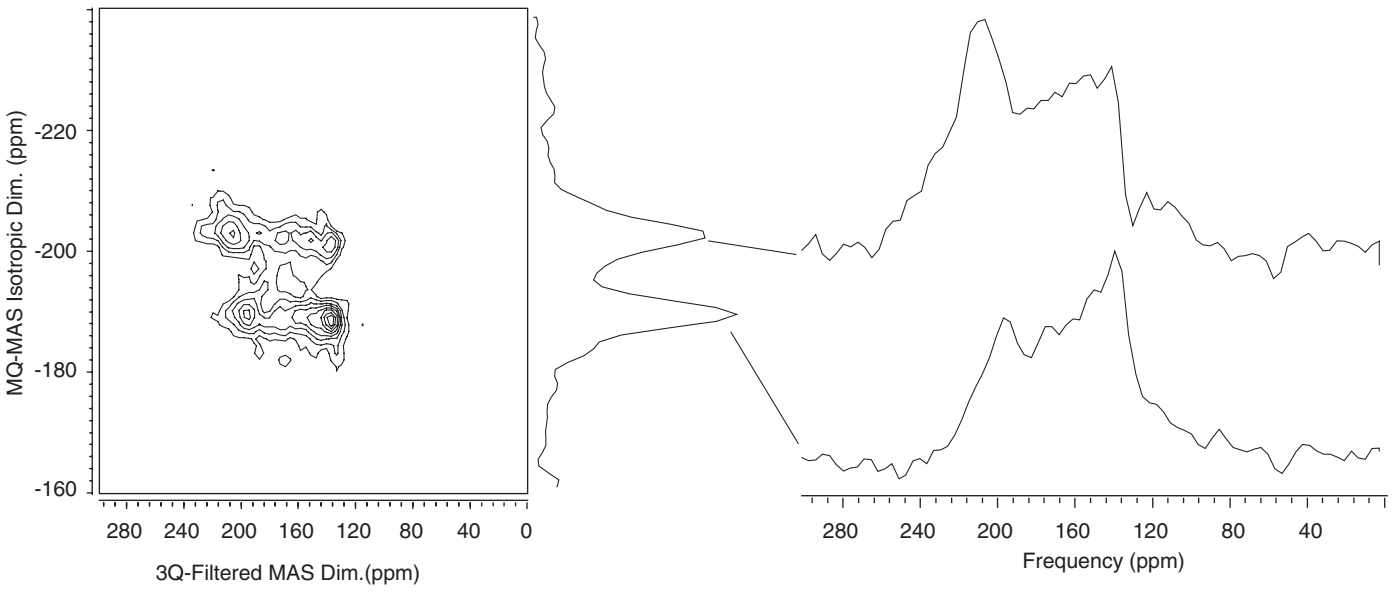

Fig. 3. ^{17}O MQ-MAS NMR spectrum of L-leucine.

4. Conclusion

Results from the numerical simulations show that the quadrupolar coupling constant (C_q) can be determined for spin $\frac{5}{2}$ nuclei by using the RAPT method. Results from experimental ^{17}O RAPT NMR and MQ-MAS NMR methods are combined to determine the quadrupolar coupling constant (C_q) and the quadrupolar asymmetry parameter (η_q) at 9.4 T. The ease by which the ^{17}O quadrupolar parameters can be obtained at relatively low magnetic field by the combination of sensitivity enhancement scheme (RAPT), fast spinning speed and resolution enhancement techniques (MQ-MAS), would accelerate the study of labelled amino acids, polypeptides, nucleosides, etc. in the solid state.

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