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17O NMR evidence for 180°-flips of (COOH)2 units in dimethylmalonic acid

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A previous 1H, 2H and 13C NMR study of dimethylmalonic acid DMMA revealed an intriguing motional process in the hydrogen bonded CO*OH-\(\ddot{\text{H}}\ddot{\text{O}}\ddot{\text{C}}\) units [1]. Considering just the hydrogens it consists of an exchange of H and \(\ddot{\text{H}}\); (II) a 180°-flip of the whole CO*OH-\(\ddot{\text{H}}\ddot{\text{O}}\ddot{\text{C}}\) unit followed by a rapid readjustment of H and \(\ddot{\text{H}}\) along the hydrogen bonds. To distinguish between the two models, we report here on 17O NMR spectra and rotation patterns recorded at \(-55^\circ C\), where the motion is frozen out, and at \(20^\circ C\), where the exchange rate is 147 kHz, from an oriented, 17O enriched single crystal of DMMA. Apart from central transitions, a host of quadrupolar split satellites appears in the \(-55^\circ C\) spectra. At \(20^\circ C\) we still observe central transitions, but virtually no satellites. By way of simulations of spectra/rotation patterns, we show that the absence of satellites in the \(20^\circ C\) spectra is not consistent with a mere exchange of H and \(\ddot{\text{H}}\). Model II leads, on the other hand, to such severe exchange broadening of the satellites at \(20^\circ C\) that they become unobservable in a real experiment. Model II is therefore consistent with our experiments and is thought to apply to DMMA. This conclusion is checked by recording spectra up to \(70^\circ C\) from a second crystal. As model II requires, coalesced and exchange narrowed satellites indeed reappear at elevated temperatures.

1. Introduction

The dynamics of hydrogens, i.e., protons or deuterons in hydrogen bonds (H-bonds) is currently a subject of active research [1-14]. These hydrogens are usually supposed to move in a double well potential with the reaction coordinate along the line connecting the bonded heavy atoms, O, N, Cl, etc., as the case may be. In crystals of many carboxylic and dicarboxylic acids the molecules are bonded by pairs of more or less parallel H-bonds in structural units of \(-\text{COOH--HOOC-}\), to be called dimeric H-bonds in what follows. These crystals are built up of dimers, chains or screws with the links provided by the dimeric H-bonds [15]. Examples are benzoic acid (dimer), malonic acid (chain) and dimethylmalonic acid, C(\(\text{CH}_3\))2(COOH)2, DMMA (screw).

The hydrogens in dimeric H-bonds have been shown by measurements and analyses of the H–H dipole–dipole coupling tensors to carry out their jumps along the H-bonds in a concerted manner [3, 5, 9]. This is schematized in figure 1(a). These jumps do not constitute, however, the only possible type of hydrogen dynamics in dimeric H-bonds. As early as 1984, K. Furić had drawn attention to an alternative process consisting of 180°-flips of the entire COOH–HOOC entities along their long axes [16]. This is shown in figure 1(b). When Furić came forward with this idea it was promptly rejected by the ETH and Kyoto NMR groups, at least as regards benzoic acid (BA): quasi-
elastic neutron scattering data from BA are inconsistent with the process shown in figure 1(b) whereas they are consistent with that shown in figure 1(a) [17, 18].

By a $^1$H, $^2$H and $^{13}$C single crystal NMR study on DMMA we were able to demonstrate in 1988 that yet another process goes on in the dimeric H-bonds of this compound [1]. Considering just the hydrogens H and H, its net result is an exchange of H and H. The rate $k = 1.47 \times 10^5 \text{s}^{-1}$ at 20°C, and the activation energy $E_a = 67 \text{kJ mol}^{-1}$ of this process turned out to be distinctly different from the rates and activation energies commonly found for hydrogen jumps along H-bonds, namely $10^{10} \ldots 10^{12} \text{s}^{-1}$ and $(8 \pm 3) \text{kJ mol}^{-1}$ [1].

Applying the techniques mentioned above, we were not able to find out how the exchange of the hydrogens takes place in DMMA. We discussed two models, I and II, which are explained in figure 2(a,b). In model I, the hydrogens exchange places while all carbon and oxygen atoms remain in their initial positions. In model II, the exchange of the hydrogens is described as a two-step process: the first step consists of a Furić type flip of the entire dimeric H-bond, while the second is a concerted jump of the hydrogens along the H-bonds. The first is supposed to take place on the rate determining slow time scale of $10^{-5} \text{s}^{-1}$ at 20°C, while the time scale of the latter should be $10^{-12} \text{s}$ or shorter. Model II implies a distinctly asymmetric potential along the H-bond. This is consistent with results of the x-ray structure determination of...
DMMA [19], inasmuch as the C═O double and C—OH single bonds appear to be localized in DMMA.

Model II differs from model I in that not only the hydrogens H and \( \tilde{H} \), but the oxygens O and \( \tilde{O} \) (and \( \tilde{O}' \) and \( \tilde{O}'' \)) exchange positions as well. As pointed out in [1], this fact can be exploited to tell apart models I and II by a \( ^{17}O \) NMR experiment. Conceptually, the most direct route would be to record first \( ^{17}O \) spectra of DMMA for a number of different crystal orientations at such low temperatures (\(- 50^\circ C \) is enough) that the motion is frozen out. In a second step, these spectra would be used to determine the \( ^{17}O \) quadrupole coupling and \( ^{17}O\text{-}^1H \) dipole–dipole coupling tensors which, in turn, would serve as input parameters for simulations of \( ^{17}O \) spectra for finite exchange rates, separately for models I and II. Remember that we know this rate for a given temperature from our previous measurements. The final step would be to compare \( ^{17}O \) spectra measured at higher temperatures with the simulations. This should allow us to discard one of the models and, hopefully, confirm the other one.

Unfortunately, we cannot follow this direct route in practice. Crystals of DMMA contain four magnetically inequivalent molecules of DMMA, which means sixteen inequivalent oxygens. The \( ^{17}O \) NMR spectrum of a single crystal therefore consists in general of \( 16 \times 5 = 80 \) resonances. The resonances come as sixteen \( m = \pm \frac{1}{2} \leftrightarrow m' = \mp \frac{1}{2} \) chemical and second order quadrupole shifted central transitions, and sixty-four \( m = \pm \frac{1}{2} \leftrightarrow m' = \pm \frac{3}{2}, m = \pm \frac{1}{2} \leftrightarrow m' = \pm \frac{1}{2} \) quadrupolar split satel-

lites. They will be further split by dipole–dipole (dd) coupling with the nearest proton neighbouring the \( ^{17}O \) nucleus. Depending on the orientation of the crystal, this splitting can be as large as 51 kHz. The total number of (possibly) resolved resonances in a \( ^{17}O \) NMR spectrum of DMMA will therefore be 160.

The consequence of this large number of resonances is that in practice it is impossible to trace out the wandering of individual transitions in rotation patterns (see below) and, thus, to determine by standard procedures the \( ^{17}O \) EFG tensors in DMMA.

What remains to be able to tell apart the motional models I and II is the following: model I affects only the \( ^{17}O\text{-}^1H \) dd splitting of the \( ^{17}O \) resonances, whereas model II affects the \( ^{17}O \) quadrupole splittings for oxygens O and \( \tilde{O} \) (\( \tilde{O} \) and \( \tilde{O}' \)), which are in the range of hundreds of kHz or even a few MHz.

We will show below that this difference has sufficiently distinct consequences to demonstrate by a comparison of measured and simulated spectra that model I can definitely be ruled out to apply for DMMA, whereas model II is consistent with our spectra. The key to success is not to consider the temperature dependence of \( ^{17}O \) spectra for only one or a few crystal orientations, but for entire rotation patterns.

2. Experimental

2.1. Synthesis of \( ^{17}O \) enriched DMMA and crystal growth

Dimethylmalonic acid was converted to dimethylmalonyl dichloride under reflux with thionyl chloride and carefully purified by two vacuum distillations. The hydrolysis back to dimethylmalonic acid (6 h at 70\(^{\circ}C \)) was carried out under exclusion of atmospheric humidity. Dimethylmalonyl dichloride (4 g) and 2 ml H\(_2\)\(^{17}O\) (Isotec Inc., Miamisburg, Ohio, USA; H\(_2\)\(^{17}O\) 48-6\%, H\(_2\)^{18}O 30-7\%) yielded 3-2 g \( ^{17}O \)dimethyl-

malonic acid. The synthesis results in the replacement of either O or \( \tilde{O} \) by a \( ^{17}O \) nucleus in 48.6\% of the CO\(^{*}\)OH groups of DMMA. Single crystals were grown at
room temperature from a solution in diethylether by very slow evaporation with tiny seed crystals.

2.2. Sample preparation

Two of the crystals, with masses 0.1674 g and 0.0222 g, respectively, were prepared as NMR samples. They will be referred to as crystal L (large) and crystal S (small). They had enough well-developed natural growth planes to allow orientating them by means of an optical goniometer. Crystal L had a somewhat elongated shape. For reasons of signal/noise in the NMR spectra we glued it on a sample holder such that it could be rotated about this long axis in the NMR coil, whose diameter of 7.7 mm was adapted to the size of the crystal.

Actually, it turned out that getting adequate signal/noise in the $^{17}$O enriched DMMA crystals is not a serious problem. We therefore chose to orientate the small crystal S such that its $\bar{d}$ axis was approximately parallel to the goniometer axis $\bar{g}$. If $\bar{d}$ was exactly parallel to $\bar{g}$, and if $\bar{g}$ was exactly perpendicular to the applied field $\bar{B}_0$, it would be possible to find rotation angles $\Psi$ such that $\bar{B}_0$ is parallel to either $\bar{c}$ or $\bar{b}$. For these situations, the $^{17}$O NMR spectra simplify in the sense that the resonances of groups of four oxygens coincide. For this to be true also for the $^{17}$O satellite resonances it is, however, necessary that $\bar{B}_0 \parallel \bar{c}$ or $\bar{B}_0 \parallel \bar{b}$ within less than 0.03°. As we cannot orientate our crystals with such precision we were content with an approximate orientation for crystal S. The actual angle subtended by its rotation axis $\bar{g}$ and $\bar{d}$ was 4.2°.

2.3. NMR

$^{17}$O NMR spectra were recorded in a field of 8.36 T using a homebuilt FT spectrometer. The $^{17}$O Larmor frequency in this field is $\nu_0 = 48.26$ MHz. Typically 120–400 free induction decays were accumulated and Fourier transformed. The repetition time between pulses was 0.5 s, which is considerably larger than the $^{17}$O spin–lattice relaxation time at all temperatures explored in this work. With the transmitter power set at 200 W, the duration of a $\pi/2$ pulse, adjusted with liquid H$_2^{17}$O (50%), was 6(±0.2)μs, which corresponds to $\omega_1 = \gamma_{17}B_1 = 2\pi \times 41.7$ kHz. As $\omega_1$ is much smaller than at least some of the $^{17}$O transitions, a $\pi/2$ pulse adjusted on a liquid sample, i.e., in the absence of (static) quadrupole interactions, will not act as a $\pi/2$ pulse on all the $^{17}$O transitions in the presence of quadrupole interactions. In fact, in the extreme case $\omega_1 \ll \Delta \omega_Q$, where $\Delta \omega_Q$ denotes the quadrupole splitting of the resonance lines, it may even act as a $\frac{1}{2} \pi$ pulse on the central transitions [20]. This leads to phasing and cancellation problems. To avoid them, we recorded $^{17}$O spectra from our crystals of DMMA with pulses of widths 2 μs and 3 μs. The sampling rate was 1 μs, implying a spectral window of ±250 kHz, which is much smaller than the total width of the $^{17}$O spectra, at least for most of the crystal orientations. In such situations, the full spectra must be recorded in slices [21]. Because we have a specific question in mind—which of the motional models I or II applies for DMMA—we confined ourselves to one single slice centred around the $^{17}$O Larmor frequency.

3. Results and discussion: model I versus model II

Figure 3(a) shows a stackplot of $^{17}$O spectra recorded for different rotation angles $\Psi$ from crystal S at −55°C. $\Psi$ was incremented in steps of 2°. The spectral range is, as mentioned above, $\nu_0 \pm 250$ kHz. An enlargement of the central section
Oxygen-17 NMR in dimethylmalonic acid

Figure 3. (a) Stackplot of $^{17}$O spectra of crystal S for different rotation angles $\Psi$, $0^\circ \leq \Psi \leq 180^\circ$. The increment of $\Psi$ is $2^\circ$. For $\Psi = 55^\circ$, $\vec{B}_0$ is parallel to the crystal axis $\vec{c}$. The spectral range is $v_0 \pm 250$ kHz. $T = -55^\circ$C. (b) Enlargement of (a) in the spectral range $v_0 \pm 75$ kHz.

$v_0 \pm 75$ kHz is shown in figure 3(b). A group of prominent peaks within the range $v_0 \pm 30$ kHz is visible at all rotation angles $\Psi$. They arise from the superposed chemical and second order quadrupole shifted central transitions of the 16 magnetically inequivalent oxygens in DMMA. Due to the strong overlapping of these lines it is, unfortunately, not possible to follow the variation with $\Psi$ of individual lines.

In addition to the central transitions, a second type of line can be recognized clearly in figure 3(a,b). They are smaller than the former and cover, for some values of $\Psi$, the entire spectral range of $v_0 \pm 250$ kHz. Without any doubt, such lines would also be found still further away from $v_0$. They represent chemically shifted, first order quadrupole split $^{17}$O satellites, split additionally by $^{17}$O-$^1$H dd couplings.

It is remarkable that such satellites do not appear at all values of $\Psi$: e.g., the range from $\Psi = 38^\circ$ to $\Psi = 78^\circ$ in figure 3(a,b) is empty of satellites within the recorded spectral slice.

Areas in the rotation pattern which are empty of satellites will be called satellite planes. The rotation pattern in figure 3(a) obviously contains two satellite planes. In section 4 we will further examine these satellite planes and draw conclusions about the $^{17}$O quadrupole coupling tensors of O and O*. Their relevance in the present context...
Figure 4. (a) Stackplot of $^{17}$O spectra of crystal S for different rotation angles $\Psi$, $0^\circ \leq \Psi \leq 180^\circ$. The increment of $\Psi$ is $2^\circ$. For $\Psi = 55^\circ$, $\vec{B}_0$ is parallel to the crystal axis $\hat{c}$. The spectral range is $v_0 \pm 250$ kHz. $T = 20^\circ$C. The arrows mark satellites (see section 4). (b) Enlargement of (a) in the spectral range $v_0 \pm 75$ kHz.

of distinguishing motional models I and II is that their very existence proves that the hosts of small lines visible in our $^{17}$O spectra outside the satellite planes are truly $^{17}$O NMR resonances and do not arise from acoustic ringing or other spurious resonances. We have further checked this point using a crystal of DMMA which was not enriched in $^{17}$O.

Despite the fact that spectra were recorded with increments of the rotation angle $\Psi$ as small as $2^\circ$ it is clearly totally impossible to follow the angular variation of individual satellites and to measure in this way the $^{17}$O quadrupole coupling tensors.

We now turn to the $^{17}$O spectra recorded from crystal S at $20^\circ$C. They are displayed in figure 4(a,b). The axes correspond to those in figure 3(a,b).

A comparison of the $-55^\circ$C rotation pattern with that for $20^\circ$C shows that the "mountain range" of central transitions essentially remained the same on increasing
Partial stick spectrum of the $^{17}$O $\frac{1}{2} \leftrightarrow \frac{3}{2}$ and $-\frac{3}{2} \leftrightarrow -\frac{1}{2}$ transitions from O and O* in DMMA, split by OH and O*H dd coupling.

Figure 5. Partial stick spectrum of the $^{17}$O $\frac{1}{2} \leftrightarrow \frac{3}{2}$ and $-\frac{3}{2} \leftrightarrow -\frac{1}{2}$ transitions from O and O* in DMMA, split by OH and O*H dd coupling.

the temperature. This becomes particularly obvious by comparing figures 3(a) and 4(a). The most striking difference between the $-55^\circ$C and $20^\circ$C rotation patterns is the fact that satellites are virtually absent in the latter. In what follows we shall exploit this difference to distinguish between motional models I and II.

We begin by considering a particular carboxylic group in DMMA with both the O and O* positions occupied by $^{17}$O nuclei. The fact that our synthesis of $^{17}$O enriched DMMA yielded COOH groups with at most one of the oxygens being an $^{17}$O does not alter the following conclusions. The advantage of considering a C$^{17}$O$^{17}$OH group is that, in connection with model II, we can truly speak of an exchange of O and O*.

We focus attention on the partial spectrum consisting of a single pair of $^{17}$O satellite transitions of O and the corresponding one of O*, say, the $\frac{1}{2} \leftrightarrow \frac{3}{2}$ and $-\frac{3}{2} \leftrightarrow -\frac{1}{2}$ transitions. Due to the magnetic inequivalence of O and O*, the quadrupole splittings $\Delta v_1$ and $\Delta v_2$ of the respective resonances will in general be different. "In general" refers to the crystal orientation. Because we do not know the quadrupole coupling tensors of O and O*, and are unable to measure them, we do not know how large $\Delta v_1$ and $\Delta v_2$ or the difference $(\Delta v_1 - \Delta v_2)$ will be. As $^{17}$O quadrupole coupling constants are typically of the order of several MHz [22] it is, however, safe to assume that the size $(\Delta v_1 - \Delta v_2)$ will be at least several hundreds of kHz for the vast majority of crystal orientations. For the following simulations of spectra we shall arbitrarily assume $(\Delta v_1 - \Delta v_2) = 800$ kHz. The quadrupole split satellite resonances of O and O* will be further split by the OH and O*H dd coupling (for the labelling of nuclei see figure 2). These splittings $\Delta v_{1,d}$ and $\Delta v_{2,d}$ depend only on the structure of the crystal (which we know from references [1] and [19] and on its orientation relative to the applied field $B_0$ (which we also know). Therefore we have complete knowledge about these additional splittings. For crystal S, the maximum of $\Delta v_{1,d}$ as a function of the rotation angle $\Psi$ is 37 kHz. The angular dependence of $\Delta v_{2,d}$ is roughly the same as that of $\Delta v_{1,d}$ but its size is only about $\frac{1}{3}$ of that of $\Delta v_{1,d}$.

The partial spectrum on which we focus attention will look, in the absence of any dynamics, like the stick spectrum in figure 5. This case applies to $-55^\circ$C. The total spectrum consists of a superposition of this partial spectrum on 7 similar ones with
Figure 6. Simulation of the evolution of the partial spectrum in figure 5 with rising temperature: (a) exchange according to model I; (b) according to model II.

Δν₁, Δν₂, Δν₁,d, Δν₁,d all being different, 8 dipolar split $\frac{1}{2} \leftrightarrow \frac{1}{2}$ and $-\frac{1}{2} \leftrightarrow -\frac{3}{2}$ satellites of O and O* each and 2.8 dipolar split central transitions. It is straightforward to calculate, as we shall do now, how the partial spectrum shown in figure 5 will change when molecular motions set in according either to model I or to model II.

**Model I, cf., figure 2(a).** Only the $^{17}$O–H dd couplings are affected by the exchange of the hydrogens H and $\bar{H}$. These couplings can be visualized as an external field effect upon the $^{17}$O resonances. The exchange therefore is equivalent to the exchange of nuclei between two chemically shifted sites. With regard to $^{17}$O–$^{1}$H dd coupling, there are two kinds of dimeric H-bonds: in the first the spin directions of H and $\bar{H}$ (quantum numbers $m_H$ and $m_{\bar{H}}$) are equal; in the second they are opposite. The two kinds of dimeric H-bonds occur in equal numbers. The $^{17}$O resonances of the first will not feel at all the exchange of H and $\bar{H}$. The respective lines remain sharp on increasing the exchange rate $k$ (the sample temperature).

The $^{17}$O resonances of the second kind of dimeric H-bond will be affected by the H–$\bar{H}$ exchange. In the partial spectrum of figure 5, the lines marked by $\pm \nu_1(m_H = +\frac{1}{2})$ and $\pm \nu_1(m_H = -\frac{1}{2})$ on the one, and $\pm \nu_2(m_{\bar{H}} = +\frac{1}{2})$ and $\pm \nu_2(m_{\bar{H}} = -\frac{1}{2})$ on the other hand will exchange broaden, coalesce and narrow again on raising the exchange rate $k$ from the slow to the fast exchange limits. The superposition of the partial $^{17}$O spectra of both kinds of dimeric H-bond will therefore evolve with rising temperature as shown in figure 6(a) (only the $\nu > \nu_0$ halves of the spectra are displayed). The decisive point to note is that satellites which are detectable in the static limit ($-50^\circ$C) must be detectable for arbitrary $k$, i.e., at any temperature.

This contradicts our observation that the satellites which we have clearly identified
as such in the \(-55^\circ\text{C}\) spectra (figure 3) are virtually absent in the \(20^\circ\text{C}\) spectra (figure 4). We take this as compelling evidence that model I cannot apply to DMMA.

The value of \(v_{1,d}\) underlying the simulations in figure 6 is the largest possible one of \(37\ \text{kHz}\) for crystal S. Our conclusion that, for model I, satellites should be observable at any temperature is valid, \textit{a fortiori}, for all other values of \(\Delta v_{1,d}\).

\textit{Model II, cf., figure 2(b).} Each oxygen retains 'its' neighbouring proton. As a result of the motion implied by this model the \(\text{O-H}\) distance changes and, hence, the magnitude of the dd splitting. This has no dramatic consequence for the \({}^{17}\text{O}\) spectrum. Far more important is the fact that oxygens \(\text{O}\) and \(\text{O}^*\) exchange sites, hence their EFG tensors, hence their quadrupole splittings \(\Delta v_1\) and \(\Delta v_2\). Note that, in the partial spectrum of figure 5, the lines from oxygen \(\text{O}\) and \(\text{O}^*\) with the same value of \(m_{\text{H}}\) and \(m_{\text{H}}\) will evolve in the familiar way on increasing \(k\). Remember that the quadrupole splittings \(\Delta v_1\) and \(\Delta v_2\) are signed. If these signs are equal, the upfield (downfield) satellite of \(\text{O}\) (with a given value of \(m_{\text{H}}\)) will exchange with the upfield (downfield) satellite of \(\text{O}^*\) (with the same value of \(m_{\text{H}}\)) while for opposite signs the exchange will be 'crosswise'.

A simulation of how the partial spectrum of figure 5 changes according to model II on increasing \(k\) or, equivalently, the temperature, is shown in figure 6(b). Again only the \(v > v_0\) halves of the (symmetric) spectra are displayed.

The decisive point to learn from figure 6(b) is that from at least \(10^\circ\text{C}\) to \(40^\circ\text{C}\) the exchange broadening of the resonances is so large that in an experimental spectrum they will certainly remain undetectable. This is in agreement with our observation that at \(20^\circ\text{C}\) virtually no satellite resonances show up in the \({}^{17}\text{O}\) spectra of crystal S of DMMA, regardless of the rotation angle \(\Psi\) of the sample. We take this as strong support that model II applies to DMMA.

One might object that our conclusions hinge on the assumption that \(\Delta v_1 - \Delta v_2 = 800\ \text{kHz}\) which underlies the simulations in figure 6. Therefore, we stress that the first conclusion—model I is inconsistent with the spectra in figures 3 and 4—is completely independent of this assumption. As regards the second—model II is consistent with the observations—it is true that the exact temperatures at which the lines disappear/reappear do depend on the above assumption. That the vast majority of satellites will be broadened by the exchange of \(\text{O}\) and \(\text{O}^*\) to an extent that they will escape detection in an appreciable temperature range will, however, remain true regardless of the particular value of \(\Delta v_1 - \Delta v_2\). Only if for some dimeric units in DMMA this difference becomes, as a function of \(\Psi\), accidentally very small, say \(20\ \text{kHz}\) or so, will the respective resonances be observable at \(20^\circ\text{C}\). The results of section 4, where we analyse the satellite planes in the \(-55^\circ\text{C}\) rotation pattern, suggest that such cases do occur, but are very rare. A closer look at figure 4(a,b) reveals indeed a few weak satellite resonances in the \(20^\circ\text{C}\) spectra at \(\Psi \approx 180^\circ\) and hints of some others at \(\Psi \approx 100^\circ\).

\textit{4. Conclusions about the \({}^{17}\text{O}\) EFG tensors in DMMA}

The rotation pattern in figure 3(a) contains two satellite planes. The very fact of their appearance, their locations and extensions will now be exploited to draw conclusions about the \({}^{17}\text{O}\) EFG tensors in DMMA. For better comparisons with the following simulations, we show in figure 7 a view 'from above' on this rotation pattern. All peaks recognized as central or satellite \({}^{17}\text{O}\) transitions in the individual spectra are marked. The narrow stripe of central transitions can be seen throughout
the rotation pattern. One satellite plane is located between $38^\circ \leq \Psi \leq 78^\circ$ and a second smaller one between $139^\circ \leq \Psi \leq 148^\circ$. In the frequency direction the boundaries of the latter extend from $v_0 - 165$ kHz to $v_0 + 165$ kHz, and are thus fully within our detected frequency range of $v_0 \pm 250$ kHz, whereas those of the former are not.

It is sufficient to consider the two EFG tensors $V$ and $V^*$ of oxygens O and O* since all others in DMMA are related to these by the elements of the space group $I4_1/acd$. The approximate local symmetry of a CO*OH group—a mirror plane—suggests that one principal direction of both $V$ and $V^*$ is perpendicular to that plane. As we shall show below, our results support this idea. The two angles $\alpha$ and $\alpha^*$ defined in figure 8 are taken to fully specify the orientations of $V$ and $V^*$. A survey of the available data on $^{17}$O EFG tensors in dimeric H-bonds was made by Gough, Haq and Smith [22]. They assumed that one of the principal axes of both $V$ and $V^*$ was perpendicular to the CO*OH plane. According to this review, the $Z$ principal axes of $V$ and $V^*$ are in the CO*OH plane with $30^\circ \leq \alpha \leq 60^\circ$ and $20^\circ \leq \alpha^* \leq 70^\circ$. The

![Figure 8](image_url)  
**Figure 8.** Orientation of the principal axes systems of the $^{17}$O EFG tensors $V$ and $V^*$ in a dimeric unit. The $Z$ and $Y$ axes are in the plane of the CO*OH group and the $X$ axes are perpendicular to it.
absolute values of the quadrupole coupling constants at O and O*, QCC and QCC*, fall in the range between 5 and 8 MHz. Depending on the particular compound to which the dimeric H-bond belongs, the asymmetry parameters η and η* of V and V* can be anywhere between 0 and 0.9. However, the available experimental data as well as calculations indicate that small asymmetry parameters, say, η, η* ≤ 0.3, are associated with a well localized C=O* double bond. Note that in DMMA the double bond is well localized [19].

To see what we can learn about V and V* from our −55° rotation pattern and its satellite planes (figures 3 and 7) we simulated such patterns making various assumptions about V and V*. The geometry of the dimeric H-bond [1], the crystal symmetry [19] and the orientation of the rotation axis of crystal S were fully taken into account. This includes the fact that the planes of the CO*OH and CO*OH groups are twisted in DMMA with respect to each other by 11.8°. Figure 9(a) shows the result of the simulation for η, η* = 0 (axially symmetric EFG tensors), |QCC| = |QCC*| = 8 MHz and α = α* = 37°. These assumptions imply that the resonances of O and O* coincide. The frequency range covers ν₀ ± 2.5 MHz. The measured spectral range of ν₀ ± 0.25 MHz is marked by two horizontal lines. Two satellite planes in the regions 15° ≤ Ψ ≤ 95° and 125° ≤ Ψ ≤ 165° appear. They are centred around Ψ = 55° and Ψ = 145°, which is in accord with the experimental finding, see figure 7. The latter plane is smaller than the former, which also agrees with the experimental data. The choice of α = α* = 37° is not arbitrary: it leads to satellite planes extending over the largest regions along the Ψ axis. The reason is that in this case the Z principal axes of all 17O EFG tensors in DMMA are parallel to the crystal c axis, hence (almost) perpendicular to the rotation axis of crystal S.

What happens when the Z principal axes of V and V* are tilted away from the plane of the CO*OH unit (by −30° and 45°, respectively) is shown in figure 9(b). Now each of the 16 magnetically inequivalent 17O sites yields a separate line, and the individual spectra become very complex. The solid curves refer to the O, O and the dashed curves to the O*, O* sites. Note that the real spectra contain even twice as many lines as the simulations, since 17O–1H dd splittings were not taken into account. No major satellite planes are visible in figure 9(b). Only two small regions void of satellites can be found. They are centred around Ψ = 125° and 165°. This case, which is typical for tilting the principal axes systems of V and V* out of the plane of the CO*OH unit, clearly does not apply to DMMA. Two satellite planes centred around Ψ = 55° and Ψ = 145°, as in the measured rotation pattern, are obtained only if the Z principal axes of V and V* are chosen to lie in the plane of the CO*OH unit, or nearly so. We thus may conclude that they are lying in that plane.

If we choose α, α* different from 37°, the extensions of the satellite planes along Ψ are reduced but their centres remain at Ψ = 55° and Ψ = 145°. Limits of α, α* consistent with the extensions along Ψ of the experimental satellite planes are 19° ≤ α, α* ≤ 55°. These limits depend (weakly) on the quadrupole coupling constants and asymmetry parameters η used for the simulations. The numbers given were derived for |QCC| = |QCC*| = 8 MHz which, according to reference [22], is an upper limit.

Figure 9(c) shows a simulation for |QCC| = |QCC*| = 8 MHz, η, η* = 0, and α = 55°, α* = 19°. The extensions of the satellite planes along Ψ have now shrunk to the size of the measured ones. However, the extension along the frequency axis of the small satellite plane is still substantially larger than actually observed. To correct for this it is necessary to give up either the idea of axially symmetric EFG tensors
Figure 9. Simulations of $^{17}$O satellite positions for crystal S as a function of $\Psi$ for various assumptions for $V$ and $V^*$. The horizontal lines mark the measured frequency window of $v_0 \pm 0.25$ MHz. Solid curves refer to the O, O and dashed curves to the O*, O* sites. (a) $QCC = QCC^* = 8$ MHz, $\eta = \eta^* = 0$, $\alpha = \alpha^* = 37^\circ$, EFG Z axes in the CO*OH plane. (b) $QCC = QCC^* = 8$ MHz, $\eta = \eta^* = 0$, $\alpha = \alpha^* = 37^\circ$, EFG Z axes of $V$ and $V^*$ tilted out of the CO*OH plane by $-30^\circ$ and $45^\circ$, respectively. (c) $QCC = QCC^* = 8$ MHz, $\eta = \eta^* = 0$, $\alpha = 55^\circ$, $\alpha^* = 19^\circ$. EFG Z axes in the CO*OH plane. (d) $QCC = 8$ MHz, $QCC^* = -8$ MHz, $\eta = 0.2$, $\eta^* = 0.6$, $\alpha = 55^\circ$, $\alpha^* = 29^\circ$. EFG Z and Y axes in the CO*OH plane.

and/or we must choose the absolute value of either $QCC$ or $QCC^*$, or of both, substantially smaller than 8 MHz. In figure 9(d) we show a simulation for $\alpha = 55^\circ$, $\alpha^* = 29^\circ$, $\eta = 0.2$, $\eta^* = 0.6$, $QCC = 8$ MHz and $QCC^* = -8$ MHz. The entire boundary of the small satellite plane is now within the measured range of $v_0 \pm 250$ kHz. If we stuck to essentially axially symmetric EFG tensors, as the review of Gough et al. [22] suggests for DMMA with its well localized C=O* double bond, we would have to assume that $|QCC|$ and/or $|QCC^*|$ is at least as small as 3 MHz. Otherwise the small satellite plane extends beyond $v_0 \pm 250$ kHz. As such small
quadrupole coupling constants are not plausible [22], we conclude that $\mathbf{V}$ or $\mathbf{V}^*$ deviate in DMMA significantly from axial symmetry.

The particular choice of the parameters for figure 9(d) is again not arbitrary: $\alpha = 55^\circ$ means that the Z principal axis of $\mathbf{V}$ is collinear to the C–O bond. Local symmetry suggests that one of the principal directions of $\mathbf{V}$ is close to this direction. $\alpha^* = 29^\circ$ implies that the Z principal axis of $\mathbf{V}^*$ is almost perpendicular to the C=O* bond, while the $X$ principal direction, corresponding to the smallest EFG absolute eigenvalue, is now along the C=O* bond. This is the orientation of the EFG tensor found by Scheubel et al. at the site of the carbonyl oxygen of benzophenone [21].

In order to check the results of our discussion in section 3, we simulated spectra and rotation patterns in the absence and presence of molecular dynamics according to models I and II, assuming the same EFG tensor parameters as for figure 9(d). The intensities of the outer and inner satellite and central transitions were taken in the ratio 5:8:9:8:5. Following the measured spectra, the linewidths were chosen as
3 kHz FWHH for both satellite and central transitions. The dipolar splittings due to the nearest neighbour $^{17}$O-1H dd interactions were also taken into account. Chemical shifts, naturally, were not taken into account. Figure 10(a) shows the result for the case where no molecular motions are present. The similarity with the experimental rotation pattern in figure 3(a) is obvious. The simulated rotation pattern for 20°C, assuming hydrogen exchange according to model I (not shown), is almost indistinguishable from figure 10(a). After the discussion in section 3 this comes as no surprise: model I does not apply to DMMA.

The simulation of $^{17}$O spectra/rotation pattern assuming motions of the dimeric unit according to model II poses a problem: strictly speaking, it is not possible to apply the "classical" line shape function in the presence of exchange (equation 2.19 of reference [23]) to the second order shifted $^{17}$O central transitions. A. Keller has given an analytical solution including second order effects of the line shape of a spin which exchanges sites [24]. Within the accuracy required for the present purposes of spectra simulations it agrees with the "classical" solution to which we shall adhere in what follows. Figure 10(b) shows the result of the simulation for 20°C. In agreement with the experimental rotation pattern, figure 4, the "mountain range" of central
transitions has changed little from the no-motion-case to 20°C where the exchange rate is 147 kHz. As a result of exchange broadening, the satellites, on the other hand, have almost completely disappeared. This is precisely our experimental finding. The simulation of figure 10(b) therefore strongly supports motional model II. It provides, moreover, credibility to the EFG tensor parameters we have chosen.

Finally, we would like to draw attention to the fact that not all satellites have vanished in the simulation for 20°C, i.e., \( k = 147 \text{ kHz} \). The reason for the survival of these satellites is obvious: there are crystal orientations for which the quadrupole splittings of particular pairs of O and O* fulfil the condition \( \frac{1}{2} | \Delta v_1 - \Delta v_2 | < k = 147 \text{ kHz} \). For the respective oxygens, the limiting case of fast exchange is then already obtained at 20°C. Satellites from such oxygens are hardly or not at all exchange broadened, and will therefore be visible in the spectrum. At the end of section 3, we mentioned that a few such satellites are also observable in the experimental 20°C rotation pattern. As the temperature is increased beyond 20°C, the fast exchange limit should be reached for more and more oxygen sites and, hence, more and more satellites should become visible. A stackplot of spectra registered for one particular orientation of crystal L at 50 different temperatures between -50°C and 70°C is shown in figure 11. The multitude of satellites visible at -50°C has vanished by and large at 10°C. Satellites reappear in new locations when the temperature is increased beyond about 20°C. This constitutes an important and necessary check of our interpretation of the virtual absence of satellite lines in the 20°C rotation pattern of crystal S, and provides further support that motional model II applies to DMMA.

5. Conclusion

We believe we have provided convincing evidence that the motional process in DMMA discovered and characterized by its kinetic parameters in reference [1] takes place according to the two-step motional model II. To the best of our knowledge, this is the first time that molecular motions which include a Furić type flip of a group as large as a COOH–HOOC unit have been demonstrated. The question which remains is: what makes DMMA peculiar among the many known carboxylic and dicarboxylic acids linked by dimeric H-bonds to allow for this process? Our answer is twofold. First, the crystal structure of DMMA provides for enough space to allow rotation of the dimeric H-bonds without significant steric hindrance. We have checked this point.
using the molecule- and crystal-building program Cosmos (written by Th. Koch, University of Jena, Germany). When rotating the dimeric H-bond, the closest contact between an oxygen and an atom of a neighbouring chain, actually a hydrogen, is 2.4 Å. This is much larger than the length of a typical O–H bond, though slightly smaller than the sum of the Van der Waals’ radii of an oxygen (1.4 Å) and a hydrogen (1.2 Å). The closest contact of the hydrogens H or \( ^1H \) with hydrogens of other chains is 2.55 Å, and is even less critical. Second, activation energies of hydrogen dynamics in carboxylic and dicarboxylic acids derived from \(^1H\) and \(^2H\) spin–lattice relaxation measurements (see table 1 of reference [1]) suggest that actually the process described by our model II is not peculiar to DMMA. O-Cl-benzoic acid and O-Br-benzoic acid are likely candidates where this process may take place as well.

References