$^1$H–$^{17}$O Nuclear Quadrupole Double Resonance in DL-Proline

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$^{17}$O nuclear quadrupole resonance spectra have been measured in an $^{17}$O enriched polycrystalline sample of DL-proline with the help of $^1$H–$^{17}$O nuclear quadrupole double resonance technique. The results show the presence of eight chemically inequivalent oxygen sites corresponding to four inequivalent proline molecules in the unit cell. The oxygen sites may be grouped into two sets of four sites. One set with short proton-oxygen distances belongs to the C–O • • • H groups whereas the other with the long proton-oxygen distances to the C = O groups.

It has been well established [1, 2, 3] that the $^{17}$O nuclear quadrupole resonance (NQR) frequencies and lineshapes provide valuable structural information on hydrogen bonded solids.

$^{17}$O has a spin 5/2 and thus has in zero magnetic field three doubly degenerate quadrupole energy levels. The corresponding NQR frequencies $v_{5/2 - 1/2} > v_{3/2 - 3/2} > v_{3/2 - 1/2}$ depend on the $^{17}$O quadrupole coupling constant $eQ_{zz}/h$ and on the asymmetry parameter $\eta = (V_{XX} - V_{YY})/V_{ZZ}$ of the electric field gradient (EFG) tensor at the site of the atom. Here $eQ$ is the $^{17}$O nuclear quadrupole moment and $V_{ij}$ the eigenvalues of the EFG tensor $(V_{ij} = \partial^2\xi / \partial X_i \partial X_j)$ with $\xi$ the electrostatic potential. The eigenvalues $V_{XX}$, $V_{YY}$, and $V_{ZZ}$ are ordered in the following way: $|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}|$.

When a hydrogen nucleus is located close to an oxygen nucleus the proton-oxygen dipolar interaction removes the degeneracy of the oxygen energy levels and the NQR lines become broad and structured. The structure of the NQR lines can be well resolved when the O–H distance is short, each oxygen molecule in the crystal is first polarized in a strong static magnetic field, which results in a smaller proton magnetic field, and then the proton spin system is in zero magnetic field. Such a resonant coupling of the two spin systems is obtained when a strong r.f. magnetic field is applied with the frequency close to an $^{17}$O NQR frequency [5]. In this case the two oxygen energy levels in the “rotating frame” couple to the proton energy levels. The oxygen system is kept “hot” in the rotating frame by sudden 180° phase shifts of the r.f. magnetic field.

When the proton-$^{17}$O distance is short, each oxygen quadrupole energy level splits into a quartet of dipolar energy levels which are dipolarly coupled to the energy levels of remaining protons. In such a case an additional relaxation of the proton system in zero

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magnetic field is obtained when the sample is simultaneously irradiated with two r.f. magnetic fields with different frequencies both within a dipolarly broadened $^{17}$O NQR line [4].

With the single-frequency irradiation technique only the NQR frequencies can be measured while the structures of the resonance lines are smeared out due to the presence of a strong r.f. magnetic field. In the two-frequency irradiation technique the r.f. powers may be much lower than in case of the single-frequency irradiation technique since the two r.f. magnetic fields are only needed to keep the spin temperature of the $^{17}$O–$^1$H groups high. Therefore with the two-frequency irradiation technique the shapes of the NQR lines can also be measured.

The sensitivities of both the single- and two-frequency irradiation techniques strongly decrease with increasing $\text{O}–\text{H}$ distance. In the former case this is due to the $^1\text{H}–^{17}\text{O}$ cross-relaxation rate which decreases with increasing $\text{O}–\text{H}$ distance, while in the latter case it is due to the heat capacity of the $^{17}$O–$^1$H groups which again decreases with increasing proton-oxygen distance.

In solid amino acids the shortest $\text{O}–\text{H}$ distances for the carboxyl ions are longer than 0.14 nm and thus the dipolar structures of the NQR lines can not be observed. It is nevertheless expected that $\text{O}–\cdots\text{H}$ interactions, especially hydrogen bonding, influence the EFG tensors and the double resonance line intensities.

In order to obtain some information on hydrogen bonding in solid DL-proline we decided to perform $^1\text{H}–^{17}\text{O}$ nuclear quadrupole double resonance measurements in an $^{17}$O enriched sample. Both the single- and two-frequency irradiation techniques have been used. The measurements have been performed at 143 K. The experimentally determined NQR frequencies and the corresponding quadrupole coupling constants and asymmetry parameters are given in Table 1.

The experimental results show the presence of eight inequivalent oxygen sites corresponding to four inequivalent proline molecules in the structure. The oxygen sites may be grouped into two sets of four sites. In set A the quadrupole coupling constants range from 6.08 MHz to 6.79 MHz and the asymmetry parameters from 0.70 to 0.17 whereas in set B the quadrupole coupling constants range from 7.72 MHz to 8.37 MHz and the asymmetry parameters from 0.24 to 0. The nuclear quadrupole double resonance lines corresponding to the oxygens of set A are stronger than the ones corresponding to the oxygens of set B.

The widths of all double resonance lines are approximately 20 kHz and the lines are not structured. We may therefore assume that the oxygens of set A correspond to the hydrogen bonded $\text{C}–\text{O}\cdots\text{H}–\text{N}$ sites while the oxygens of set B correspond to the $\text{C} = \text{O}$ sites with the shortest $\text{O}–\cdot\cdot\cdot\text{H}$ distance much longer than in case of the A-sites. Within the set A the intensities of the double resonance lines only slightly decrease with increasing quadrupole coupling constant while within the set B the double resonance lines corresponding to the sites B1 and B2 are significantly stronger than the double resonance lines corresponding to the sites B3 and B4, i.e. the shortest proton-oxygen distances are for the sites B1 and B2 somewhat shorter than for the sites B3 and B4.

Since the crystal structure of DL-proline is not known we may relate the double resonance data to the structure of 4-hydroxy-L-proline [6] where the carboxyl ion is bound with two different $\text{O}–\cdot\cdot\cdot\text{H}–\text{N}$ hydrogen bonds. One of the two oxygens is bound with a strong intermolecular hydrogen bond ($R(\text{O}–\cdot\cdot\cdot\text{H}) = 0.1695$ nm) while another oxygen is bound with a somewhat weaker intramolecular hydrogen bond ($R(\text{O}–\cdot\cdot\cdot\text{H}) = 0.2082$ nm). A possible explanation of the double resonance data for the oxygens of set B is that there are two molecular conformations present in the structure: one (sites B1 and B2) in which the intramolecular hydrogen bond is present and another (sites B3 and B4) without the intramolecular hydrogen bond.

The two quadrupole coupling constants as well as the two asymmetry parameters of a carboxyl ion mainly depend on the electron charge distribution within the ion. The $^{17}$O NQR data in solid DL-proline show rather large variations of the quadrupole

<table>
<thead>
<tr>
<th>Site</th>
<th>$v_{3/2-1/2}$ (kHz)</th>
<th>$v_{3/2-3/2}$ (kHz)</th>
<th>$v_{5/2-1/2}$ (kHz)</th>
<th>$eQV_{zz}/h$ (kHz)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1050(10)</td>
<td>2025(10)</td>
<td>3075(10)</td>
<td>6790(20)</td>
<td>0.170(3)</td>
</tr>
<tr>
<td>A2</td>
<td>1150(10)</td>
<td>1870(10)</td>
<td>3020(10)</td>
<td>6450(20)</td>
<td>0.436(2)</td>
</tr>
<tr>
<td>A3</td>
<td>1290(10)</td>
<td>1725(10)</td>
<td>3015(10)</td>
<td>6170(20)</td>
<td>0.663(2)</td>
</tr>
<tr>
<td>A4</td>
<td>1310(10)</td>
<td>1690(10)</td>
<td>3000(10)</td>
<td>6080(20)</td>
<td>0.703(2)</td>
</tr>
<tr>
<td>B1</td>
<td>1230(10)</td>
<td>2290(10)</td>
<td>3520(10)</td>
<td>7720(20)</td>
<td>0.242(2)</td>
</tr>
<tr>
<td>B2</td>
<td>1195(10)</td>
<td>2325(10)</td>
<td>3520(10)</td>
<td>7780(20)</td>
<td>0.150(3)</td>
</tr>
<tr>
<td>B3</td>
<td>1250(10)</td>
<td>2485(10)</td>
<td>-</td>
<td>8280(20)</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>B4</td>
<td>1250(10)</td>
<td>2510(10)</td>
<td>-</td>
<td>8370(20)</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>
coupling constants and asymmetry parameters within set \( A \) as well as within set \( B \). This may be related to different resonance structures of the carboxyl group in which the electron charge is readily distributed between the two \( C-O \) bonds by a variety of mechanisms including hydrogen bonding, substituent effects and molecular vibrations [7]. We believe that in case of a carboxyl ion the electron charge distribution depends mainly on the difference of the two \( O-H \) interaction strengths. \(^{17}\text{O} \) NQR data in carboxylic acids [7] show a nearly linear correlation of the quadrupole coupling constants at the \( C-O-H \) sites with the quadrupole coupling constants at the \( C=O \) sites. A correlation of the quadrupole coupling constants with the asymmetry parameters has also been found for the \( C-O-H \) sites as well as for the \( C=O \) sites. In DL-proline the correlation of the quadrupole coupling constant with the asymmetry parameter is for the strongly hydrogen bonded sites \( A \) nearly the same as for the \( C-O-H \) sites in carboxylic acids while it is for the sites \( B \) nearly the same as for the \( C=O \) sites in carboxylic acids. The correlation of the \(^{17}\text{O} \) quadrupole coupling constants at the sites \( A \) with the \(^{17}\text{O} \) quadrupole coupling constants at the sites \( B \) can not be studied since it is at present not clear which site of the set \( A \) and which site of the set \( B \) correspond to the same carboxyl ion. Further \(^{17}\text{O} \) NQR measurements in solid amino acids are needed to find this correlation which may help us in the assignment of the oxygen sites.