$^1H-^{17}O$ 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 polycristalline sample of DL-proline with the help of $^1H-^{17}O$ 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 the short proton-oxygen distances belongs to the $C-O \cdots H$ 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 $\nu_{5/2-1/2} > \nu_{5/2-3/2} \geq \nu_{3/2-1/2}$ depend on the ^{17}O quadrupole coupling constant eQV_{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_{XX}, V_{YY}, and V_{ZZ} are the eigenvalues of the EFG tensor $(V)_{ij} = \partial^2 V/\partial x_i \, \partial x_j$ with V 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 shorter than approximately 0.14 nm. In such a case the O–H distance as well as the orientation of the O–H bond in the eigenframe of the EFG tensor can be determined from the widths and shapes of the ^{17}O NQR lines [3, 4].

Since a) the ^{17}O NQR frequencies are typically below 4 MHz, b) the natural concentration of the isotope ^{17}O is 0.037% and c) in hydrogen bonded solids the ^{17}O NQR lines are broad, the ^{17}O NQR spectra are usually measured with the help of the $^1H-^{17}O$ nuclear quadrupole double resonance technique based on magnetic field cycling [4]. Here the proton system is first polarized in a high static magnetic field. Then the static magnetic field is adiabatically reduced to zero resulting in a significant decrease of the proton spin temperature. In zero magnetic field the proton spin temperature approaches the temperature of the sample at a rate determined by the spin-lattice relaxation time in zero magnetic field $T_1(0)$. When after a time τ spent in zero magnetic field the static magnetic field is increased to the initial value, the remaining proton magnetization is smaller than the initial proton magnetization by the factor $\exp\{-\tau/T_1(0)\}$. A faster relaxation of the proton spin system in zero magnetic field, which results in a smaller proton magnetization at the end of the magnetic field cycle, occurs when the proton system is in zero magnetic field resonantly coupled to a "hot" oxygen system. 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 O$-$H distance. In the former case this is due to the ^{1}H$-^{17}$O cross-relaxation rate which decreases with increasing O$-$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 O$-$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 O $\cdots$ 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}H$-^{17}$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 ar 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**.

Table 1. ^{17}O NQR frequencies, quadrupole coupling constants and asymmetry parameters in solid DL-proline at 143 K.

Site	$\nu_{3/2-1/2}$ (kHz)	$\nu_{5/2-3/2}$ (kHz)	$\nu_{5/2-1/2}$ (kHz)	eQV_{ZZ}/h (kHz)	η
A1	1050(10)	2025(10)	3075(10)	6790(20)	0.170(3)
A2	1150(10)	1870(10)	3020(10)	6450(20)	0.436(2)
A3	1290(10)	1725(10)	3015(10)	6170(20)	0.663(2)
A4	1310(10)	1690(10)	3000(10)	6080(20)	0.703(2)
B1	1230(10)	2290(10)	3520(10)	7720(20)	0.242(2)
B2	1195(10)	2325(10)	3520(10)	7780(20)	0.150(3)
B3	1250(10)	2485(10)	–	8280(20)	<0.1
B4	1250(10)	2510(10)	–	8370(20)	<0.05

The widths of all double resonance lines are approximately 20 kHz and the lines are not structured. We may therefore assume that the oygens of set **A** correspond to the hydrogen bonded C$-$O $\cdots$ H$-$N sites while the oxygens of set **B** correspond to the C$=$O sites with the shortest O $\cdots$ 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 **B**1 and **B**2 are significantly stronger than the double resonance lines corresponding to the sites **B**3 and **B**4, i.e. the shortest proton-oxygen distances are for the sites **B**1 and **B**2 somewhat shorter than for the sites **B**3 and **B**4.

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 O $\cdots$ H$-$N hydrogen bonds. One of the two oxygens is bound with a strong intermolecular hydrogen bond ($R(\mathrm{O} \cdots \mathrm{H}) = 0.1695$ nm) while another oxygen is bound with a somewhat weaker intramolecular hydrogen bond ($R(\mathrm{O} \cdots \mathrm{H}) = 0.2082$ 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 **B**1 and **B**2) in which the intramolecular hydrogen bond is present and another (sites **B**3 and **B**4) 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 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}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}O quadrupole coupling constants at the sites **A** with the ^{17}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}O NQR measurements in solid amino acids are needed to find this correlation which may help us in the assignment of the oxygen sites.

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