^{1}H–^{17}O Nuclear-Quadrupole Double-Resonance Study of Hydrogen Disorder in 2-Nitrobenzoic Acid

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Temperature dependence of ^{17}O nuclear quadrupole resonance frequencies was measured in solid 2-nitrobenzoic acid by a ^{1}H–^{17}O nuclear quadrupole double resonance technique. The experimental results show the presence of a fast exchange of hydrogen atoms between two nonequivalent positions within the O–H . . . O hydrogen bonds. The hydrogen disorder is ascribed to concerted jumps of two hydrogen atoms within the hydrogen bonds connecting two molecules in a dimer. The energy difference ΔE of the two hydrogen configurations is equal to $\Delta E = 60$ meV $= 5.8$ kJ/mol. The dipole structure of the ^{17}O NQR lines from the C–O–H oxygen positions was also measured at $-100°C$ and at room temperature. The orientation of the principal axes of the electric field gradient tensor with respect to the O–H bond and the sign of the quadrupole coupling constant were determined. The oxygen–hydrogen distance $R_{\text{O-H}}$, as determined from the dipole structure of the ^{17}O NQR lines is at $-100°C$ equal to 0.099 nm. At room temperature we observe a longer distance, $R_{\text{O-H}} = 0.101$ nm, in agreement with the hydrogen intrabond exchange. © 2000 Academic Press

Key Words: NQR; double resonance; electric field gradient; hydrogen bond; carboxylic acid.

INTRODUCTION

Molecules of benzoic acid and substituted benzoic acid form centrosymmetric dimers in the solid state. The two molecules of a dimer are bound with two equivalent O–H . . . O hydrogen bonds. The length of a hydrogen bond is close to 0.265 nm.

A significant degree of hydrogen disorder has been observed in solid carboxylic acid dimers. The hydrogen disorder has been interpreted in two ways. Either the eight-membered hydrogen bonded ring (Fig. 1) performs 180°-flips around the C–C axis (*1*) or the two hydrogen atoms in the two hydrogen bonds perform concerted jumps O–H . . . O ↔ O . . . H–O (*2–4*). The experimental data (*5, 6*) support the model of concerted jumps with the exception of dimethylmalonic acid where the 180°-flips have been observed (*7*).

Hydrogen disorder in benzoic acid, 4-nitrobenzoic acid, and 4-hydroxybenzoic acid has been recently studied analyzing the

temperature variation of the ^{17}O nuclear quadrupole resonance (NQR) frequencies (*6*). This study shows that the hydrogen disorder in the above three compound is indeed high. The two hydrogen configurations of a hydrogen bonded dimer are not energetically equivalent. The energy difference ΔE of the two hydrogen configurations is low, on the order of 1 kJ/mol. In 4-nitrobenzoic acid ΔE does not vary with temperature, whereas in 4-hydroxybenzoic acid and in benzoic acid ΔE decreases with increasing temperature.

The molecules of 2-nitrobenzoic acid also form dimers in the solid state (*8*). A hydrogen bonded dimer is schematically shown in Fig. 1. The length of the hydrogen bonds, i.e., the oxygen–oxygen distance $R_{\text{O. . .O}}$, is equal to $R_{\text{O. . .O}} = 0.2645$ nm. The position of the two nitro groups makes the two possible hydrogen configurations of the eight-membered hydrogen bonded ring nonequivalent. It is not known if the hydrogen atoms are disordered also in 2-nitrobenzoic acid.

In order to check the possibility of hydrogen disorder and to obtain some structural data and NQR parameters regarding the O–H . . . O hydrogen bonds we performed the measurement of ^{17}O NQR frequencies in dependence of temperature. In addition, we measured the dipole structure of the ^{17}O NQR lines at a low temperature and at room temperature.

EXPERIMENTAL TECHNIQUE

^{17}O has a spin 5/2 and thus in zero magnetic field three doubly degenerate quadrupole energy levels. Their energies depend on two parameters: the quadrupole coupling constant e^2qQ/h and the asymmetry parameter η of the electric field gradient (EFG) tensor. The EFG tensor is a symmetric traceless second rank tensor composed of the second derivatives of electrostatic potential with respect to coordinates. It has three real principal values V_{XX}, V_{YY}, and V_{ZZ}, ($|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}|$). The quadrupole coupling constant $e^2qQ/h = eQV_{ZZ}/h$ is the product of the nuclear quadrupole moment eQ and the largest principal value V_{ZZ} of the EFG tensor divided by the Planck constant h. The asymmetry parameter η is equal to $\eta = (V_{XX} - V_{YY})/V_{ZZ}$. It ranges between 0 and 1.

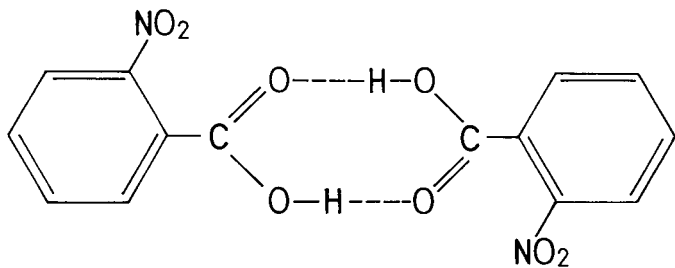The three NQR frequency are named as $\nu_{5/2–1/2}$, $\nu_{5/2–3/2}$, and

FIG. 1. Scheme of 2-nitrobenzoic acid.

$\nu_{3/2-1/2}$; $\nu_{5/2-1/2} > \nu_{5/2-3/2} \geq \nu_{3/2-1/2}$. All three transitions are allowed, except for $\eta = 0$ when the high frequency transition corresponds to $\Delta m = 2$ and cannot be induced by a rf magnetic field. The two NQR parameters, e^2qQ/h and η, can be extracted from the NQR frequencies. Since the EFG tensor depends on the electric charge distribution around the ^{17}O nucleus, NQR distinguishes between the C–O–H oxygen position and the C=O . . . H oxygen position.

When a hydrogen nucleus ($I = \frac{1}{2}$) is placed close to a ^{17}O nucleus the dipole–dipole interaction removes the double degeneracy of the nuclear quadrupole energy levels and the double degeneracy of the proton ground state in zero magnetic field. Each quadrupole energy energy level splits into a quartet (9, 10). A NQR line thus consists in principle of 16 dipole lines. The dipole lines are not sharp due to the dipole–dipole interaction with the rest of hydrogen nuclei. The dipole structure of a NQR line is therefore partially smeared out and the structure of a NQR line can be expressed by the line shape function $g(\nu)$. Since the dipole–dipole interaction strongly varies with the oxygen hydrogen distance R_{OH}, $H_D \propto 1/R_{OH}^3$, we obtain at the C–O–H oxygen position broad ^{17}O NQR lines and at the C=O . . . H oxygen position narrow ^{17}O NQR lines. This helps us in assigning the NQR lines. A precise measurement of the dipole structure of the NQR lines gives in addition the O–H distance R_{OH}, the sign of the quadrupole coupling constant and the orientation of R_{OH} in the principal-axes coordinate system of the EFG tensor (9, 10).

The natural concentration of ^{17}O is 0.037%. It is therefore hard to observe its NQR frequencies by conventional NQR techniques, especially in the case of a strong oxygen–hydrogen dipole–dipole interaction, which strongly broadens the ^{17}O NQR lines. We therefore used a field cycling nuclear quadrupole double resonance technique. Here ^{17}O is observed via its influence on the hydrogen (proton) NMR signal.

The sample is first kept in a strong static magnetic field B_0 for several proton spin–lattice relaxation times. During this time a thermal equilibrium between the proton spin system and crystal lattice is reached. Then the magnetic field is adiabatically reduced to zero. The Zeeman order of the proton spin system is adiabatically transfered into the dipolar order and the spin temperature of the proton spin system drops by nearly four orders of magnitude. After a time τ spent in zero magnetic field the initial magnetic field B_0 is adiabatically restored. The dipolar order transforms back into the Zeeman order and a nuclear magnetization M appears. The proton NMR signal is measured immediately after B_0 is restored. It is proportional to M.

During the time τ spent in zero magnetic field the spin–lattice interaction tends to establish a thermal equilibrium between the proton spin system and crystal lattice. The proton spin temperature approaches the temperature of the sample exponentially with the characteristic time $T_1(0)$, which is called the proton spin–lattice relaxation time in zero magnetic field. The proton spin–lattice relaxation in zero magnetic field reduces the magnetization M, which reappears in the proton spin system when the magnetic field B_0 is adiabatically restored. The proton NMR signal S at the end of the magnetic field cycle decreases with increasing τ as $S = S_0\exp(-\tau/T_1(0))$.

A faster relaxation of the proton spin order in zero magnetic field, and as a result a lower proton NMR signal S, is obtained when the "cold" proton spin system in zero magnetic field resonantly interacts with a "hot" oxygen spin system.

A strong rf magnetic field with the amplitude B_1 and with the frequency ν equal to a ^{17}O NQR frequency ν_Q induces in the oxygen spin system a splitting of the energy levels $\Delta\nu$, $\Delta\nu \approx \gamma_O B_1/2\pi$. Here γ_O is the gyromagnetic ratio of a ^{17}O nucleus. This splitting is analogous to the splitting of the energy levels in the rotating frame, as observed in NMR. In contrast to NMR we obtain in a polycrystalline sample a distribution of $\Delta\nu$. The value of $\Delta\nu$ namely depends on the orientation of the rf magnetic field in the principal axis frame of the EFG tensor. An appropriate choice of B_1 sets a typical value of $\Delta\nu$ equal to the width of the proton resonance line in zero magnetic field. This is how the resonance interaction of the two spin systems is established. If the rf magnetic field is off-resonance, $\nu = \nu_Q \pm \Delta$, the resonance frequency in the rotating frame increases. It is approximately equal to $\Delta\nu \approx [(\gamma_O B_1/2\pi)^2 + \Delta^2]^{1/2}$. When Δ exceeds the width of the proton NMR line in zero magnetic field, the resonance interaction of the two spin systems is strongly reduced.

The flip–flop transitions in the two resonantly interacting spin systems tend to equalize their spin temperatures. The oxygen spin system which has in general low heat capacity strongly cools down, whereas the spin temperature of the proton spin system only slightly increases. In order to keep the oxygen spin system "hot" and to allow a continuous flow of energy from the oxygen spin system to the proton spin system we use sudden 180° phase shifts of the rf magnetic field (11). Each phase shift inverts the population of the two closely split oxygen energy levels transforming the oxygen spin temperature to a negative value.

A shortening of the proton spin–lattice relaxation in zero magnetic field is observed only when $\nu \approx \nu_Q$. If this is not the case, the proton–oxygen resonance interaction is strongly reduced and the effect of the 180° phase modulation of the rf magnetic field on the population of the two closely split energy

levels in the off-resonance "rotating frame" becomes weak. The NQR frequencies are searched by repeating magnetic field cycles at fixed τ and at different values of the frequency ν and measuring the proton NMR signal S. The ν-dependence of the proton NMR signal S at the end of the magnetic field cycle exhibits dips around $\nu = \nu_Q$.

In the present experiment, the sample was pneumatically moved between two magnets with the transfer time of 0.1 s. In the first magnet, the proton Larmor frequency was equal to 32 MHz, whereas in the second magnet the external magnetic field was compensated ($B < 0.05$ mT). The time spent in the high and zero magnetic field was 60 and 0.5 s, respectively. The amplitude and modulation frequency of the rf magnetic field were equal to 3 mT and 2 kHz, respectively.

The dipole structure of the ^{17}O NQR lines was measured using double resonance with coupled multiplets (9). Here the proton spin system in zero magnetic field resonantly interacts with the dipole energy levels of the ^{17}O–H groups. In zero static magnetic field we apply two weak rf magnetic fields. The frequency ν_1 of the first rf magnetic field is usually fixed close to an edge of the structured NQR line. The line is scanned with the frequency ν_2 of the second rf magnetic field, which changes in steps between repetitive magnetic field cycles. When both ν_1 and ν_2 lie within the same diploarly broadened and structured ^{17}O NQR line we observe a continuous flow of energy from the ^{17}O–H groups to the proton spin system. The increase of the proton relaxation rate ΔW depends on the NQR line shape function $g(\nu)$ as $\Delta W \propto g(\nu_1) g(\nu_2)$. In addition, ΔW quadratically depends on the frequency difference $\nu_1 - \nu_2$. With ν_1 fixed at the lower end of the NQR line, the scan with ν_2 gives the dipole structure of the upper part of the NQR line. The dipole structure of the lower part of the NQR line is obtained with a second scan with ν_1 fixed at the upper end of the NQR line.

In the present experiment the parameters of a magnetic field cycle were the same as before whereas the amplitudes of the two rf magnetic fields were significantly lower, $B_1 = B_2 = 0.3$ mT.

RESULTS AND DISCUSSION

The ^{17}O NQR frequencies were measured using 180° modulation of the rf magnetic field. The modulation frequency was equal to 2 kHz and the amplitude B_1 of the rf magnetic field was equal to $B_1 = 3$ mT. The polarization time of the proton spin system in the high magnetic field B_0, $B_0 \approx 0.8$ T, was equal to 60 s and the time τ spent in zero magnetic field was equal to 0.5 s.

The temperature dependence of the ^{17}O NQR frequencies $\nu_{5/2-3/2}$ and $\nu_{3/2-1/2}$ is shown in Fig. 2. The full circles represent the NQR frequencies from the C=O oxygen positions, whereas the open circles represent the NQR frequencies from the C–O–H oxygen positions. The assignment has been made on the basis of line widths. As seen from Fig. 2, the NQR frequencies exhibit a strong nonlinear dependence on temperature.
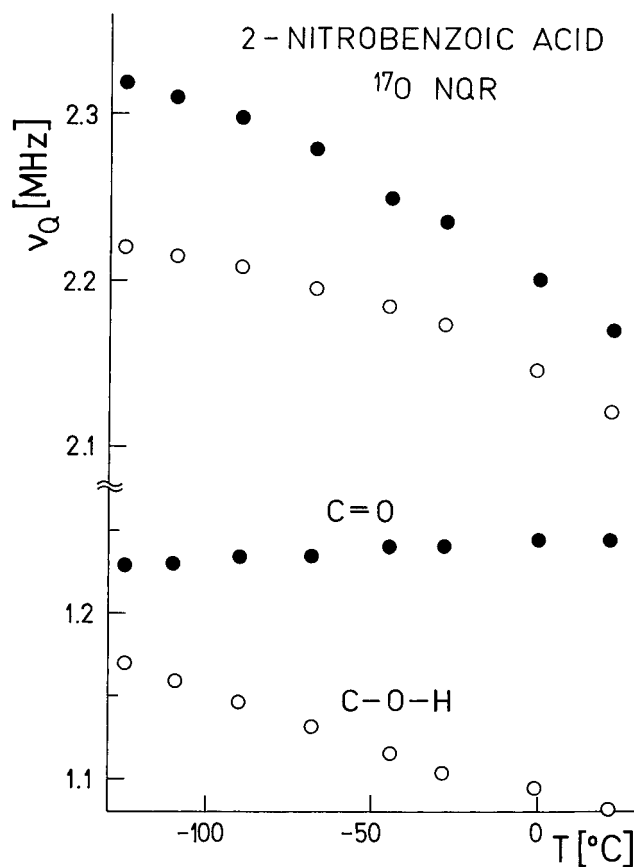

FIG. 2. Temperature dependence of ^{17}O NQR frequencies $\nu_{5/2-3/2}$ and $\nu_{3/2-1/2}$ in 2-nitrobenzoic acid.

The temperature dependence of the absolute values $|e^2qQ/h|$ of the quadrupole coupling constants and the asymmetry parameters η is shown in Fig. 3. At a C=O oxygen position the absolute value of the quadrupole coupling constant varies between 7.8 MHz at $-125°$C and 7.4 MHz at room temperature. The asymmetry parameter η varies between 0.21 at $-125°$C and 0.35 at room temperature. At a C–O–H oxygen position $|e^2qQ/h|$ varies between 7.5 MHz at $-125°$C and 7.1 MHz at room temperature, whereas η varies between 0.20 at $-125°$C and 0.12 at room temperature.

The temperature variation of $|e^2qQ/h|$ and η is strong and nonlinear. It shows the presence of rather large temperature dependent fluctuations of the EFG tensor at both the C=O and C–O–H oxygen positions. The fluctuations are fast on the NQR time scale, $\omega_Q \tau_c \ll 1$. Here ω_Q is a characteristic ^{17}O NQR frequency ν_Q, $\nu_Q \sim 1$ MHz, multiplied by 2π. No characteristic features associated with the slowing down of the fluctuations ($\omega_Q \tau_c \rightarrow 1$), like homogeneous line broadening and fast quadrupole spin–lattice relaxation, is observed between $-125°$C and room temperature. Also, the proton spin–lattice relaxation time at $\nu_L = 32$ MHz and in zero magnetic field shows no shortening, which is usually associated with the slowing down of fluctuations. We assume that these fluctuations originate
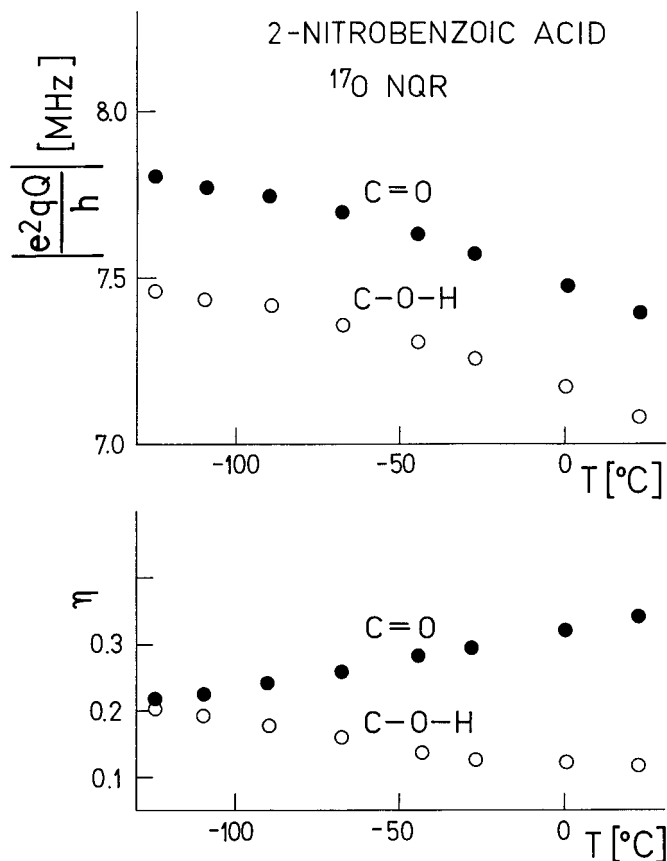
FIG. 3. Temperature dependence of the ^{17}O quadrupole coupling constants and asymmetry parameters in 2-nitrobenzoic acid.

from a fast exchange between two nonequivalent hydrogen configurations of the eight-membered hydrogen bonded central ring. The characteristic time τ_c of the fluctuations is much shorter than 10^{-8} s. In such a case we experimentally observe a time-averaged EFG tensor. Let P represent the probability of finding the central ring in the energetically lower hydrogen configuration. It is equal to $P = 1/(\exp(-\Delta E/k_B T) + 1)$, where ΔE is the energy difference of the two hydrogen configurations. We further define the hydrogen order parameter S as $S = 2P - 1$. The order parameter S is in case of a complete order ($P = 1$) equal to 1, whereas it is in case of a complete disorder ($P = \frac{1}{2}$) equal to zero. The time-averaged EFG tensors $\langle V \rangle$ at the C=O and C–O–H oxygen positions read in terms of the hydrogen order parameter as

$$\langle V(C = O) \rangle = \frac{1 + S}{2} V(C = O) + \frac{1 - S}{2} V(C-O-H)$$

$$\langle V(C-O-H) \rangle = \frac{1 + S}{2} V(C-O-H) + \frac{1 - S}{2} V(C = O).$$

$$[1]$$

Here $V(C = O)$ and $V(C-O-H)$ represent the static values of

the EFG tensor at the C=O and C–O–H oxygen positions, respectively.

As concluded on the basis of the previously published data and theoretical considerations one of the principal axes of the EFG tensor points nearly perpendicular to either the C–O–H plane or the C=O . . . H plane (*12*). We call the principal value of the EFG tensor along this out-of-plane principal axis V_{33}. In the case of a hydrogen exchange in an O–H . . . O hydrogen bond the direction of the out-of-plane principal axis at a given oxygen position does not vary in time. In order to determine the energy difference ΔE and the static values $V_{33}(C=O)$ and $V_{33}(C-O-H)$ we may therefore instead of the tensor equations [1] use scalar equations

$$\langle V_{33}(C = O) \rangle = \frac{1 + S}{2} V_{33}(C = O)$$

$$+ \frac{1 - S}{2} V_{33}(C-O-H)$$

$$\langle V_{33}(C-O-H) \rangle = \frac{1 + S}{2} V_{33}(C-O-H)$$

$$+ \frac{1 - S}{2} V_{33}(C = O). \qquad [2]$$

In the case of a benzoic acid dimer and substituted benzoic acid dimers with the hydrogen bond length of approximately 0.265 nm the out-of-plane principal value V_{33} of the EFG tensor is V_{XX} at the C=O oxygen position and V_{YY} at the C–O–H oxygen position. The ^{17}O quadrupole coupling constant is at the C–O–H oxygen position negative, whereas at the C=O oxygen position it is positive (*6, 12*).

The temperature variation of $\langle V_{33}(C=O) \rangle$ and $\langle V_{33}(C-O-H) \rangle$, both multiplied by eQ/h, is shown in Fig. 4a. At the C–O–H oxygen position $\langle eQV_{33}/h \rangle$ decreases from 4.50 MHz at $-125°C$ to 3.85 MHz at room temperature. At the C=O oxygen position $\langle eQV_{33}/h \rangle$ increases from -3.10 MHz at $-125°C$ to -2.45 MHz at room temperature. The sum $\langle eQV_{33}(C=O)/h \rangle + \langle eQV_{33}(C-O-H)/h \rangle$ is equal to 1.41 MHz. It is temperature independent in agreement with expressions [2]. The difference $\langle eQV_{33}(C-O-H)/h \rangle - \langle eQV_{33}(C=O)/h \rangle$ is proportional to the hydrogen order parameter S. Its temperature dependence can be used to determine the energy difference ΔE of the two hydrogen configurations and the static values $eQV_{33}(C=O)/h$ and $eQV_{33}(C-O-H)/h$. The best agreement with the experimental data is obtained if $\Delta E = 60$ meV = 5.8 kJ/mol, $eQV_{33}(C=O)/h = -3.14$ MHz, and $eQV_{33}(C-O-H)/h = 4.55$ MHz. The last two values are close to the values obtained from the correlation diagram in Ref. (*12*), which correlates the out-of-plane principal values of the EFG tensor and the length of the hydrogen bond. Figure 4b shows the temperature dependence of the hydrogen order parameter S as determined from the difference $\langle eQV_{33}(C-O-H)/h \rangle - \langle eQV_{33}(C=O)/h \rangle$.
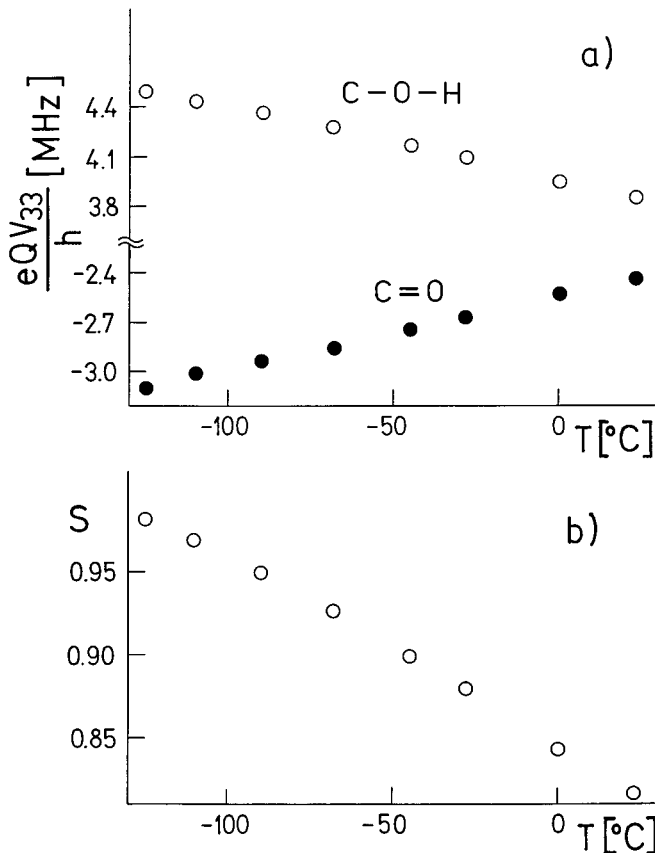
FIG. 4. Temperature dependence of the out-of-plane principal values of the EFG tensor multiplied by (a) eQ/h and of the hydrogen order parameter (b) S.

Knowing the energy difference ΔE one can, using expressions [1] from the experimentally determined temperature dependence of the time-averaged ^{17}O quadrupole coupling constant at the C=O and C–O–H oxygen positions (Fig. 3), calculate their static values and the angle γ between the principal axis Z at a given oxygen position when the hydrogen atom is close to the oxygen atom (O–H) and the principal axis Z when the hydrogen atom is far (O . . . H). The best agreement with the experimental data is obtained when $\gamma = 75°$, $eQ\mathbf{V}_{zz}(\text{C=O})/h = 7.83$ MHz and $eQ\mathbf{V}_{zz}(\text{C–O–H})/h = -7.50$ MHz.

The dipole structure of the ^{17}O NQR lines from the C–O–H oxygen position was measured at $-100°$C and at $25°$C using double resonance with coupled multiplets. Spectra showing the dipole structure of the NQR line corresponding to the $\frac{3}{2}-\frac{1}{2}$ transition are shown in Fig. 5. At both temperatures, $R_{\text{O-H}}$ lies in the X–Z plane of the EFG tensor forming an angle of $55° \pm 5°$ with the principal axis Z. The quadrupole coupling constant is negative. These results confirm that the out-of-plane principal axis at the C–O–H position is indeed the Y axis and that $\mathbf{V}_{33} = \mathbf{V}_{YY} > 0$.

The oxygen–hydrogen distance $R_{\text{O-H}}$ as determined from the dipole structure of the ^{17}O NQR lines is at $-100°$C equal to $R_{\text{O-H}} = (.099 \pm 0.001)$ nm. At room temperature we obtain

$R_{\text{O-H}} = (.101 \pm 0.001)$ nm. The two distances seem to be equal within the experimental error, but they are not. The experimental error is mainly caused by the partial smearing of the dipole structure of the NQR line caused by the dipole–dipole interaction with the rest of hydrogen nuclei. The NQR lines are at $-100°$C by 5% broader than at room temperature, as seen also in Fig. 5. If we assume that the hydrogen exchange model is valid then the above technique gives the time-averaged oxygen–hydrogen distance R defined as (13, 14)

$$\frac{1}{\mathbf{R}^3} = \mathbf{P}\,\frac{1}{\mathbf{R}_{\text{O-H}}^3} + (1 - \mathbf{P})\,\frac{1}{\mathbf{R}_{\text{O.\,.\,.H}}^3}. \qquad [3]$$

Taking into account the energy difference ΔE, $\Delta E = 60$ meV = 5.8 kJ/mol, of the two hydrogen configurations as obtained from the temperature dependence of the ^{17}O NQR frequencies and the hydrogen bond length $R_{\text{O.\,.\,.O}}$, $R_{\text{O.\,.\,.O}} = R_{\text{O-H}} + R_{\text{O.\,.\,.H}} = 0.265$ nm we obtain a good agreement between the experimentally determined oxygen–hydrogen distances and expression (3) if $R_{\text{O-H}} = (0.099$ nm $\pm 0.001)$ nm. Here we assume that the O–H . . . O hydrogen bond is linear ($\angle$O–H . . . O $= 180°$). Small deviation

^{1}H– ^{17}O DOUBLE RESONANCE IN 2-NITROBENZOIC ACID

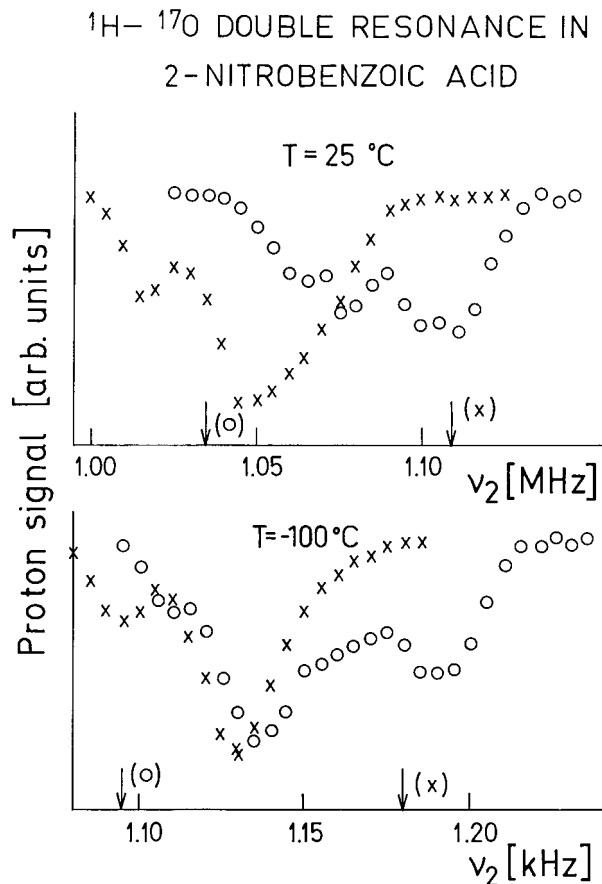**FIG. 5.** Dipole structure of the ^{17}O NQR line corresponding to the 3/2–1/2 transition at $-100°$C and $25°$C as obtained by the two-frequency irradiation. The arrows represent the fixed frequency ν_1.
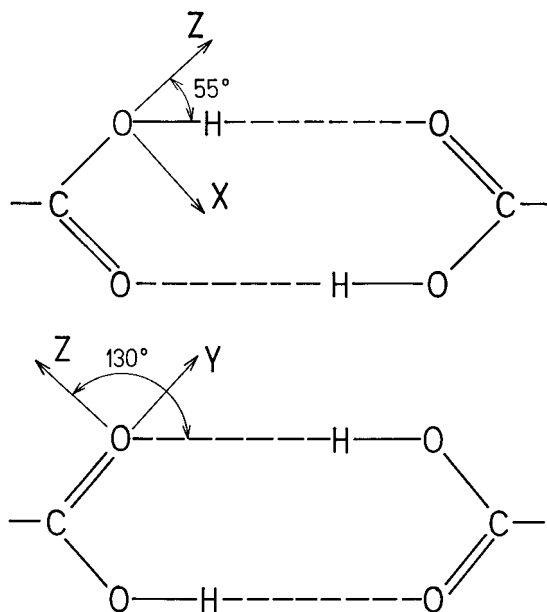
FIG. 6. The most probable orientation of the principal axes of the EFG tensor at the C–O–H oxygen position and at the C=O . . . H oxygen position.

from the linearity, as generally observed in the O–H . . . O hydrogen bonds, does not change our conclusion. The temperature variation of the widths of the ^{17}O NQR lines agrees with the model of concerted hydrogen jumps.

The most probable orientation of the principal axes of the EFG tensor at the C–O–H and C=O oxygen positions is shown in Fig. 6. At the C–O–H oxygen position, the Z axis forms an angle of 55° with the O–H bond as determined from the dipole structure of the ^{17}O NQR lines. At a given oxygen position the angle γ between the Z axis in case of a close hydrogen (O–H) and the Z axis in case of a distant hydrogen (O . . . H) is equal to 75° as determined from the temperature dependence of the time-averaged EFG tensor. Thus in case of a distant hydrogen the most probable angle between the Z principal axis and the O . . . H direction is 130°. These results are close to those previously observed in related hydrogen bonded systems (5).

It is worth noting what we expect in case of a 180° reorientation of the eight-membered hydrogen bonded ring. First, the out-of-plane principal axis reorients for 180° what does not change the principal value V_{33} of the EFG tensor. Thus a temperature independent principal value V_{33} is expected. In the case of the C–O–H oxygen position, where the orientation of the principal axis Z with respect to the O–H bond is experimentally determined, we expect a fluctuation of the principal axis Z between two orientations separated by 110° (Fig. 6). Such a fluctuation strongly affects the two in-plane principal values of the EFG tensor. A similar outcome is true also for the C=O oxygen position. These expectations disagree with the experimental observations. ^{17}O NQR thus supports the model of concerted hydrogen jumps.

In addition, 180°-flips of molecules strongly modulate the in-

termolecular proton dipole–dipole interaction. As a result we expect a strong influence of this motion on the proton spin–lattice relaxation time. Several years ago we made an attempt to determine the ^{17}O NQR frequencies in dimethylmalonic acid where the molecules are indeed performing 180°-flips. Unfortunately, the proton spin–lattice relaxation time is close to the zero magnetic field very short, much shorter than 0.1 s, which is necessary to perform a double resonance experiment. We observed such a short proton spin–lattice relaxation time, which is most probably due to the 180° molecular flips, in a broad temperature region between −130°C and room temperature. In contrast to dimethylmalonic acid, we observe in solid benzoic acid and substituted benzoic acid long proton spin–lattice relaxation times, which only weakly vary with temperature.

CONCLUSIONS

Strong temperature variation of the ^{17}O NQR frequencies has been observed in solid 2-nitrobenzoic acid. The temperature variation of the principal values of the EFG tensor, as determined from the NQR frequencies, is in agreement with the model of concerted jumps O–H . . . O ↔ O . . . H–O of hydrogen atoms in two hydrogen bonds connecting a hydrogen bonded dimer. The two hydrogen configurations of the eight-membered hydrogen bonded ring are not energetically equivalent. The energy difference ΔE, $\Delta E = 60$ meV = 5.8 kJ/mol, in a 2-nitrobenzoic acid dimer is larger compared to ΔE in a benzoic acid dimer and in parasubstituted benzoic acid dimers. ΔE is also temperature independent. The large value of ΔE in 2-nitrobenzoic acid is presumably the consequence of the position of the substituent, which makes the two oxygen atoms in an O–H . . . O hydrogen bond nonequivalent.

The characteristic time of the concerted proton jumps is much shorter than 10^{-8} s.

Measurement of the dipole structure of the ^{17}O NQR lines from the C–O–H oxygen position gave the oxygen–hydrogen distance, which is at −100°C, equal to $R_{O-H} = (0.099 \pm 0.001)$ nm. At room temperature, we observe 5% narrower ^{17}O NQR lines, this corresponds to an increase in the oxygen–hydrogen distance of 0.002 nm. The increase of the oxygen–hydrogen distance is assumed to be dynamic nature. A fast motion of a hydrogen atom between two nonequivalent positions within an O–H . . . O hydrogen bond partially averages out the ^{1}H–^{17}O magnetic dipole–dipole interaction.

The ^{17}O quadrupole coupling constant at the C–O–H oxygen position is observed to be negative. The principal value Y of the EFG tensor points perpendicular to the C–O–H plane. The most probable orientations of the principal axes of the EFG tensor at the C–O–H oxygen position and at the C=O oxygen position are deduced from the dipole structure of the ^{17}O NQR lines and from the temperature dependence of the principal values of the EFG tensor.

It is shown that a 180° reorientation of the eight-membered hydrogen bonded ring around the C–C axis does not affect the

out-of-plane principal value V_{33} of the EFG tensor, whereas the two in-plane principal values are strongly affected. ^{17}O NQR data do not support this model.

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