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NMR Study of Dynamics of Carboxyl Proton in Crystals of Acetylenedicarboxylic Acid and *p*-Nitrobenzoic Acid

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Two kinds of motions of proton in dimeric carboxyl group were distinguished by the temperature dependence of spin-lattice relaxation times of dipolar system (T_{1d}) and of Zeeman system (T_{1z}) on acethylenedicarboxylic acid (ADCA) and on *p*-nitrobenzoic acid (PNBA) in the *A2/a* form. High temperature motion of ADCA is 180° rotation of the eight-membered ring of dimeric carboxyl group about the axis nearly parallel to the hydrogen bonds. The activation energy of this motion of ADCA is 58 kJ mol^{-1}. The low temperature motion of ADCA and PNBA is the proton translation along the hydrogen bonds in a dimeric carboxyl group, which induces the minima of T_{1z} and T_{1d} at the same temperature. The activation energy derived from the high temperature slope of T_{1z} curve is 6.9 kJ mol^{-1} for ADCA and 2.5 kJ mol^{-1} for PNBA. The low temperature slope gives a small activation energy of 1.9 kJ mol^{-1} for ADCA and 1.0 kJ mol^{-1} for PNBA. The frequency dependence of T_{1z} in the low temperature limit was constant at low Larmor frequency. This result indicates that the translational motion of protons along the hydrogen bonds is not classical but quantum-mechanical.

Coupled motion of atoms, radicals, or molecules in solids is one of very interesting problems of molecular dynamics. We have been interested in the rotational tunneling of methyl groups in solids for some time.[1] In many cases, there are evidences of coupling of such motion between neighboring methyl groups. The strength of this coupling is considered to be determined primarily by the spacial proximity of neighboring methyl groups.

In the case of the eight-membered ring of carboxyl group dimer, two tautometric forms may exist by alternating the chemical bonds (single and double bonds) and the hydrogen bonds as shown in Fig. 1. Two hydrogen atoms in such an eight-membered ring must move in a concerted way along the hydrogen bonds during the alternation, i.e. the motion of the hydrogens must be a coupled transfer. The configurations, I and II, have the same energy in the isolated state (i.e. in gas phase) but in general have different energies in the solid state due to interaction with other molecules. Thus, the configurations can not be distinguished in the gas phase,[2] whereas different populations between I and II are seen in the solid state.[3]

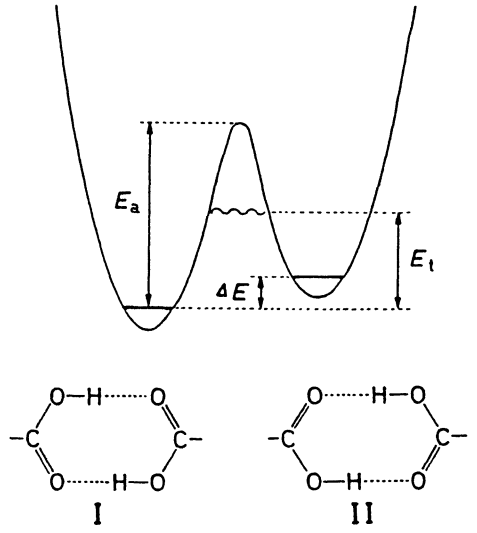

Fig. 1. Schematic view of double minimum potential of proton translation in a dimeric carboxyl groups and two corresponding configurations.

In recent years, the dynamics of protons in the carboxyl group dimers in solids has been investigated by nuclear magnetic resonance[4-6] and neutron scattering methods.[7-9] Meier et al.[4] and Nagaoka et al.[6] found a broad, shallow minimum in the temperature dependence of the proton spin-lattice relaxation time of the Zeeman system T_{1z} for several carboxylic acid dimers. This spin-lattice relaxation behavior can not be interpreted in terms of a classical, simultaneous hopping motion of the two protons between the unequal potential wells which correspond to the states I and II. For example, the activation energy derived from the low temperature side of the T_{1z} minimum is smaller than that from the high temperature side, contrary to the prediction that classical hopping motion of protons must result in a steeper slope of T_{1z} on the low temperature side of the minimum than on the high temperature side. Meier et al. and Nagaoka et al. assigned this T_{1z} minimum to the concerted translational motion of the protons along the hydrogen bonds in the eight-membered ring and also suggested that the quantum-mechanical tunneling effect played an important role in this motion. The temperature dependence of the correlation time of the translational motion of protons was explained by Meyer and Ernst[10] by the pocket state model of the tunneling motion. A preliminary model of the spin-lattice relaxation due to this tunneling mode was proposed by Nagaoka et al.[6] but the detailed nature of the spin relaxation due to tunneling is not known. We are much interested in the tunneling dynamics of the protons in this system and in particular what features will appear in the observables of the

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NMR as a result of such proton tunneling. Thus, we report in this paper several remarkable properties of observables of NMR, i.e. spin-lattice relaxation time of the Zeeman system (T_{1z}) and of the dipolar system (T_{1d}) and the shape of the absorption line for acetylenedicarboxylic acid and *p*-nitrobenzoic acid. Nagaoka et al.[6] also measured T_{1z} of *p*-nitrobenzoic acid but they dealt with a polymorphic phase different from the one of the present study.

The conversion between the states I and II in Fig. 1 is also possible by another mechanism, i.e. 180° rotation about the long axis, which is claimed by Furic.[11] There has been some controversy about the mechanism by which the conversion occurs. The initial and final states are the same in both mechanisms for some observables but the nature of the processes and the relevant energy level structure will be very different from each other.

Experimental

Materials. Acetylenedicarboxylic acid (hereafter called ADCA) was purchased from Tokyo Chemical Industry, Co., Ltd. and was further purified. Two kinds of samples were prepared. One was purified by recrystallization from dry diethyl ether solution in an evacuated closed system, keeping the specimen away from humidity. The other was purified by vacuum sublimation from 360 K onto a 273 K tip. Chemical analysis gave the relative masses, C 42.02%, H 1.83%; calculated for $C_4H_2O_4$: C 42.12%, H 1.78%. The differential thermal analysis of this specimen showed no peaks between 77 and 440 K. For the NMR measurements, these specimens were degassed in the glass ampules which were sealed off with helium gas of 2 kPa for heat exchange. Raman scattering experiment was performed on the recrystallized specimen which was sealed into a glass capillary with helium gas at 50 kPa.

p-Nitrobenzoic acid (PNBA) was purchased from Nakarai Chemicals and was recrystallized three times from methanol solution. Small single crystals were obtained. Analysis gave C 50.13%, H 2.97%, N 8.30%; calculated for $C_7H_5NO_4$ were C 50.31%, H 3.02%, N 8.38%.

Two polymorphic forms of PNBA have been known with the space groups, $P2_1/c$ (a=5.043, b=5.153, c=24.692 Å, β=96.89°, Z=4)[12] and $A2/a$ (a=12.918, b=5.042, c=21.298 Å, β=96.66°, Z=8).[13] The specimen we used for the NMR measurements was identified to be the $A2/a$ modification from the lattice parameters, a=12.9, b=5.04, c=21.2 Å and β=95°, from the X-ray Weissenberg photograph. It was confirmed by powder X-ray diffraction that the recrystallized PNBA was clearly different from sublimed PNBA in structure, the latter being used by Nagaoka et al. for their NMR measurements.[6] Here, we note that the differential thermal analysis of sublimed specimen showed a very small exothermic peak at about 100 K in the cooling direction, whereas the recrystallized specimen showed no anomaly between 80 and 510 K.

There was a suspicion that the sublimed specimen was in a metastable phase, which was transformed into a more stable form on cooling. An attempt to detect the thermal anomaly in the heating direction of DTA was not successful because it is the region of large drift in the DTA output. However, the diffraction pattern of a sublimed PNBA that had been anealed at 77 K was the same as that of the virgin sublimed sample. Therefore, the thermal anomaly as seen in the sublimed PNBA at about 100 K must be due to a reversible phase transition. The recrystallized specimen was pulverized and it was treated in the same way as for ADCA for NMR and Raman experiments.

Measurements. The proton spin-lattice relaxation time of the Zeeman system (T_{1z}) was measured by the 90° train-τ-90° pulse sequence; the relaxation times obtained by this method were confermed to be the same as those by the 180°-τ-90° method at several temperatures above 77 K. The length of 90° pulse was typically 1.3 μs. The dependence of T_{1z} on the intensity of external field was measured by the field cycling technique.[1] The spin-lattice relaxation time of the dipolar system (T_{1d}) was measured by the $90°_x$-t-$45°_y$-τ-$45°_y$ pulse sequence. The T_{1z}-process and T_{1d}-process of ADCA and PNBA could be expressed by a single exponential function except in the very low temperature region of ADCA. The absorption line shapes of ADCA and PNBA were recorded by the home-built Robinson type and Pound-Watkins type spectrometers. The width of field modulation was $2H_m$=0.85 G**. The temperature of the specimen was automatically kept constant within ±0.1 K during a measurement and was measured by a Chromel-P-Constantan thermocouple above 15 K and by Au/Fe-Chromel-P thermocouple and a germanium resistance thermometer below 15 K.

Results and Discussion

Identification of Two Types of Molecular Motions and 180° Rotation of Dimeric Carboxyl Group.

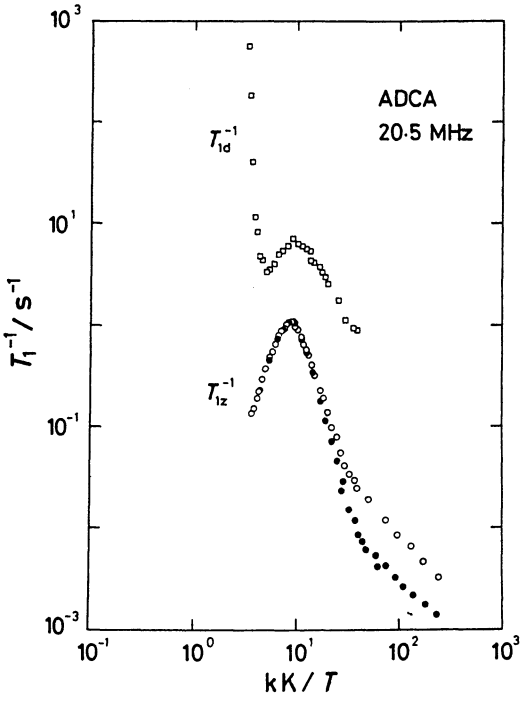

Fig. 2. Log-log plot of the spin-lattice relaxation rates of Zeeman system (○, ●) and of dipolar system (□) of acetylenedicarboxylic acid vs. inverse temperature. ○, □ are for recrystallized sample and ● is for sublimed sample.

** 1G=10^{-4}T.

A. Acetylenedicarboxylic Acid. T_{1z}^{-1} and T_{1d}^{-1} curves of ADCA are shown in Fig. 2. Open circles and open squares are, respectively, T_{1z}^{-1} and T_{1d}^{-1} of the recrystallized specimen and closed circles are T_{1z}^{-1} of the sublimed specimen. It was found that the absolute values of T_{1z}^{-1} in the low temperature region ($T<25$ K) depended on the method of preparation. This result suggests that the relaxation process below 25 K is not an intrinsic property of ADCA crystal. We will shortly discuss the low temperature relaxation. The magnetization recovery was described by two exponential functions, i.e. fast relaxing component and slowly relaxing component, rather than by a single exponential function. We derived T_{1z}^{-1} (ex.) from the slowly relaxing component, because the magnetization of fast relaxing component was only about 20% of equilibrium value even at 4.2 K and disappeared at about 15 K. T_{1z}^{-1} (ex.) varied linearly with $H_0^{-1/2}$ (H_0: external magnetic field) and with T. We thus subtracted the extrapolated value of this extrinsic contribution from the observed relaxation rate (T_{1z}^{-1} (obs.)) to obtain the intrinsic relaxation rate (T_{1z}^{-1} (in.)) above 25 K,

$$T_{1z}^{-1}\text{ (in.)} = T_{1z}^{-1}\text{ (obs.)} - T_{1z}^{-1}\text{ (ex.)}. \quad (1)$$

T_{1z}^{-1} (in.) and T_{1d} are shown in Fig. 3. There are two types of molecular motions which are effective on T_{1d} in different temperature regions. We will now consider three types of motions of protons in a dimeric carboxyl groups. These are (i) coupled translation of the two protons along the hydrogen bonds in a dimeric unit, (ii) 180° rotation of this eight-membered ring about the axis nearly parallel to the hydrogen bonds, and (iii) proton diffusion from a dimer to another. Only the motion (i) of these three modes has a low enough potential barrier to induce "quantum-mechanical motion." It is noted that the minima of T_{1z} and T_{1d} occur at about the same temperature, 110 K in the case of ADCA (Fig. 3) and 70 K in the case of PNBA, as will be described below. This behavior cannot be expected from any classical random motion. Such a nonclassical behavior of the spin relaxation in the low temperature region will be discussed in detail in the following section (*Quantum mechanical behavior of*···). In contrast, the high temperature behavior of T_{1z} and T_{1d} must arise from slow classical motion because a much larger activation energy is involved. Therefore, it is reasonable to assess that the low temperature motion is of type (i) and high temperature motion is of either type (ii) or (iii); it may be possible to decide on the latter from the line shape measurement.

Typical differential absorption lines of ADCA at several temperatures are reproduced in Fig. 4. The width of the central line, which became observable at a higher temperature, was determined by the width of field modulation even if the modulation width was made as small as possible ($2H_m<0.1$ G). The intensity of this narrow component depended on the method of preparation of the sample, i.e. the intensity of recrystallized specimen was about 30 times larger than that of sublimed specimen. We ignore the contribution of this narrow component to the second moment for the moment and come back to this point in section C. The line shape below 150 K did not depended on the method of preparation.

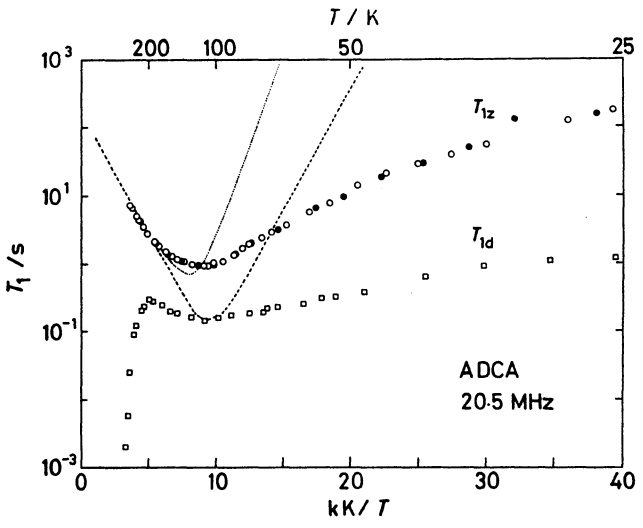

Fig. 3. Temperature dependence of the spin-lattice relaxation times of Zeeman system (○, ●) and of dipolar system (□). The extrinsic contribution to observed T_{1z}, which is seen in the low temperature region ($T<25$ K) in Fig. 2, are subtracted. The broken and dotted curves are the calculated T_{1z} for ΔE=0.2 kJ mol^{-1} and for ΔE=2.9 kJ mol^{-1}, respectively (see in the text).

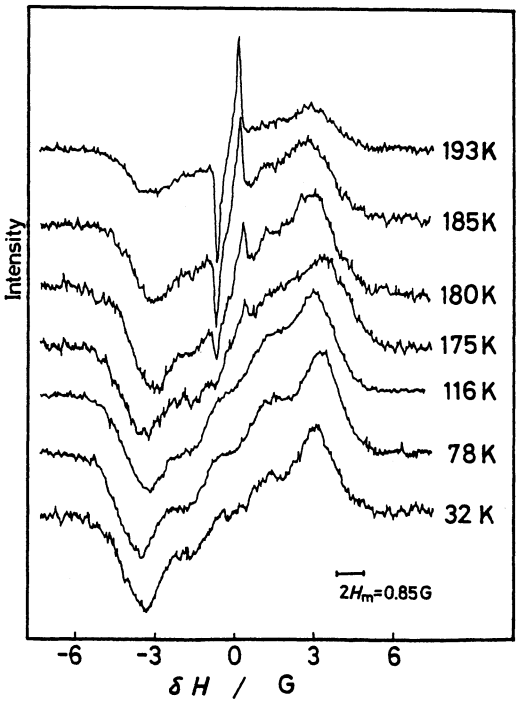

Fig. 4. The typical differential absorption line of recrystallized acetylenedicarboxylic acid at several temperatures.

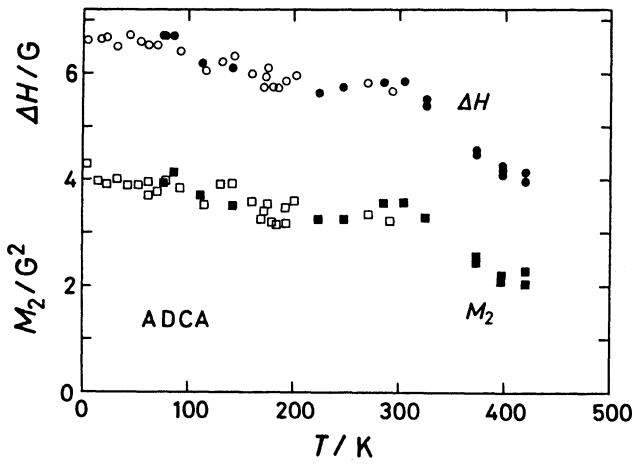

Fig. 5. The temperature dependence of maximum slope width (○, ●) and second moment (□, ■) of acetylenedicarboxylic acid; ○, □ are for the recrystallized sample and ●, ■, are for the sublimed sample.

The temperature dependences of the maximum slope width (ΔH) and the second moment (M_2) are shown in Fig. 5. The reduction of second moment (ΔM_2) due to 180° rotation of the eight-membered ring was estimated as follows. The rigid lattice value of the second moment of ADCA was calculated to be M_2 (rigid)=3.53 G^2 or 2.03 G^2 by using the formula,[14]

$$M_2\,(\text{rigid}) = (3/5)\,\gamma^4\hbar^2\,\mathrm{I(I+1)}\sum_{j,k} 1/R_{jk}^6. \qquad (2)$$

taking into account only the intradimer contribution. The distance between the two protons within a dimeric unit is known to be R_I=2.37 Å in one configuration and R_II=2.16 Å in the other by the X-ray diffraction experiment[15] as shown in Fig. 6. It was also shown by X-ray diffraction that the configuration with a proton distance of 2.37 Å has somewhat larger population.[15] The angle θ between the two proton vectors (see Fig. 6) is 51.6°.[15] As temperature is increased, the dipolar interaction between the two protons becomes partially averaged by the low temperature motion, fast coupled translation of the two protons along the hydrogen bonds. Therefore, the averaged orientation of the proton-proton vector can be chosen as indicated by the broken line in Fig. 6. The angle ϕ depends on the temperature and on the energy difference ΔE indicated in Fig. 1. The value of ΔE will be discussed in the following section (*Classical picture*). The magnitude of intradimer contribution to ΔM_2 that arises from the 180° rotation was estimated to be less than 0.5 G^2 by assuming that the two potential minima of the rotation have the equal depth. The observed reduction, 1 G^2, which also includes the contribution from the interdimer interaction, is close to the estimate. The diffusion of protons from a dimeric acid unit to another in the crystal should cause a very large decrease in the second moment but there is no such indication in Fig. 5. Thus the high temperature motion of ADCA is the 180° rotation of dimeric carboxyl groups. The activation energy of this motion is 58 kJ mol^{-1} which was obtained from the slope of T_{1d}.

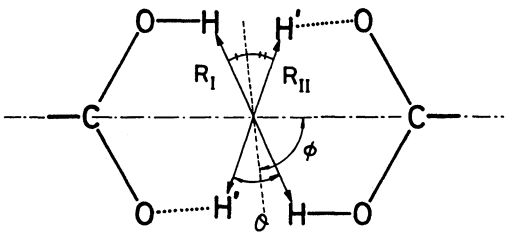

Fig. 6. The configuration of a dimeric carboxyl groups with two possible orientations of a proton-proton vector.

B. *p*-Nitrobenzoic Acid. The spin-lattice relaxation times, T_{1z} and T_{1d}, of PNBA are shown by closed circles and open squares, respectively, in Fig. 7. T_{1z} values measured at 59.53 MHz by Nagaoka et al.,[6] which are for the sublimed $P2_1/c$ modification, are also shown (○). The discrepancy between the T_{1z} values by us (●) and those by Nagaoka et al. (○) is clearly due to different polymorphic forms. It appears that the temperature variation of T_{1z} and $T_{1d}$of PNBA and that of ADCA are similar to each other (compare Figs. 3 and 7). There are also two types of molecular motions which are effective on T_{1d} in different temperature regions as in the case of ADCA and the minima of T_{1z} and T_{1d} at 70 K correspond to the translational motion of proton in a dimeric carboxyl group.

The differential line shape and maximum slope

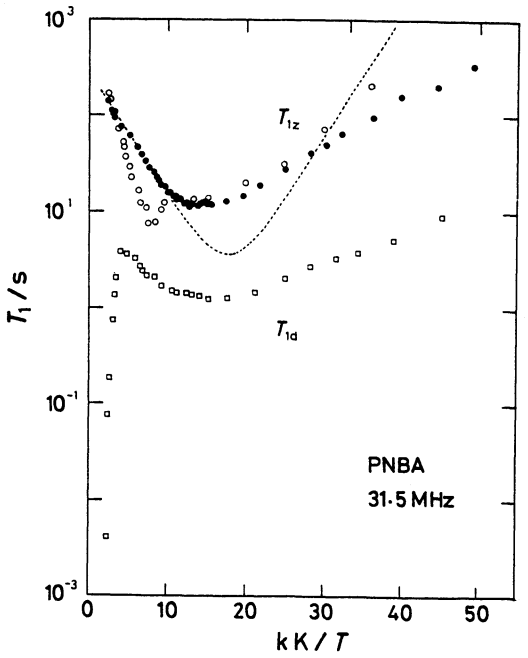

Fig. 7. Temperature dependence of spin-lattice relaxation times of Zeeman system (○, ●) and of dipolar system (□) of *p*-nitrobenzoic acid. ○ is observed at 59.53 MHz by Nagaoka et al.[6] The broken curve is the calculated T_{1z} from the classical formula (see in the text).

width of PNBA are shown in Figs. 8 and 9, respectively. The line shape of PNBA was very different from that reported by Gupta and Saxena.[16] Unlike the case of ADCA, the line width of PNBA stays constant up to 300 K. The apparent activation energy derived from the high temperature slope of T_{1d} of PNBA was 80 kJ mol^{-1}, larger than in the case of ADCA. The steep decrease of T_{1d} at high temperatures was observed for several carboxylic acid dimers and was attributed to the excitation of 180° flip motion of the dimer structure by Chiba for the first time.[17]

C. Narrow Component of Absorption Line of Acetylenedicarboxylic Acid. The narrow component of absorption line was observed at high temperature for sublimed and recrystallized ADCA as described above. It was also observed for α-oxalic acid at high temperature[18] but not for PNBA. The intensity of the narrow component of recrystallized and sublimed ADCA was reproducible during the several cycles of heating and cooling experiments. The narrow component was not due to any gaseous decomposition products because outgassing of the glass ampule did not change its intensity. The molecules of ADCA and oxalic acid have two carboxyl groups on both ends of a molecule (the head and the tail), which makes the exsistence of free carboxyl groups on certain crystal surface very plausible. In contrast, there will be no free carboxyl groups on the crystal surface of PNBA. Assuming that free carboxyl groups adsorb water strongly and, as a result, acid protons can migrate on the surface through hydrogen bonds, the narrow component of differential absorption line may be explained. From the temperature coefficient of the relative peak intensity (height) of this narrow component of the differential absorption line an energy difference of 20 kJ mol^{-1} was derived between the protons in the mobile state and in the static state for the recrystallized ADCA, which is close to the energy of an O-H···O hydrogen bond. The same value was obtained for the sublimed ADCA. Hence, the dependence of the intensity of narrow component on the method of preparation may be attributed to a difference in the water adsorbed area of the surface of the crystals.

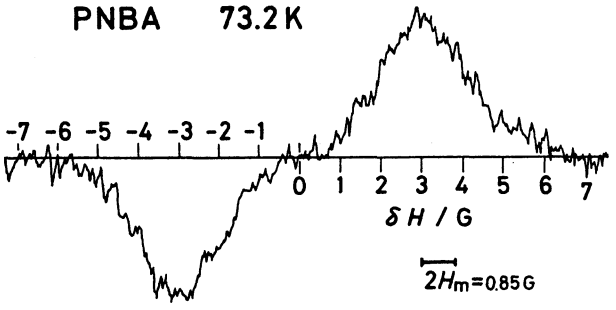

Fig. 8. The typical differential absorption line of *p*-nitrobenzoic acid.

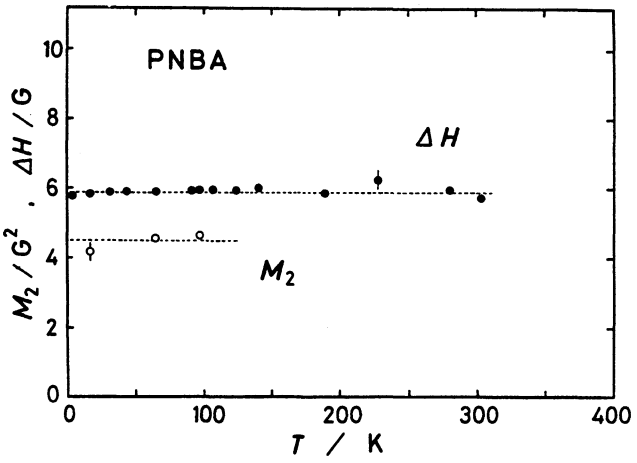

Fig. 9. Temperature dependence of the maximum slope width and second moment of *p*-nitrobenzoic acid.

Proton Translation Along the Hydrogen Bonds in a Dimer of Carboxyl Groups. A. Classical Picture. The translational motion of the two protons within a dimer of carboxyl group is probably the cause of the minimum of T_{1z} and T_{1d} as inferred in the preceding section. The temperature dependence of T_{1z} of PNBA and ADCA is very similar to that of other carboxylic acid dimers.[4-6] We will first attempt to calculate T_{1z} by a classical treatment of proton translation and compare the result of such calculation with the observed T_{1z}.

The spin-lattice relaxation formula due to classical hopping between unequal potential wells was derived[6]*** from a general expression of spin relaxation by Soda.[19] In general, T_{1z}^{-1} is given by

$$T_{1z}^{-1} = mC \sum_l A_l \, \mathrm{B}(\tau_{cl}). \tag{3}$$

The sum is taken over the normal modes l of the molecular motion.[19] The coefficient, $C=(9/4)\gamma^4\hbar^2$, is the spin part of the dipolar interaction between the two protons and A_l is the structure-dependent coefficient for the normal mode l. The coefficient m denotes the fraction of the proton spins which relax directly due to motion among the total proton spins present in the crystal. In the present case of the dimeric carboxyl group, we take into account completely coupled translation of the two protons along the hydrogen bonds. T_{1z}^{-1} is then given by

$$T_{1z}^{-1} = mCA\mathrm{B}(\tau_c) \tag{4}$$

where

$$B(\tau_c) = \tau_c/(1+\omega_0^2\tau_c^2) + 4\tau_c/(1+4\omega_0^2\tau_c^2)$$

$$A = (2/15)\,[a/(a+1)^2]\,[R_{\mathrm{I}}^{-6} + R_{\mathrm{II}}^{-6} + (1-3\cos^2\theta)R_{\mathrm{I}}^{-3}R_{\mathrm{II}}^{-3}]$$

$$a = \exp(\Delta E/RT)$$

$$\tau_c = [\tau_{c0}/(a+1)]\exp(E_a/RT).$$

R_i denotes the distance between the two protons in the i-th configuration and θ is the angle between the proton-proton vector of configurations I and II. Equa-

*** There is an error in the coefficient of Eq. 16 of Ref. 6.

tion 4 is of the same form as that given by Meier et al.[4] in the limit that $R_I=R_{II}$ and $\Delta E \ll E_a$ except for the coefficient A.

The values, ΔE, E_a, R_I, R_{II}, and θ which are necessary for the calculation of T_{1z}^{-1}, were obtained as follows. The energy difference (ΔE) between the two configurations of ADCA was derived from the temperature dependence of the integrated intensity of the Raman bands (O-H stretching vibrations; 2240 and 2280 cm^{-1}). Supposing that these two bands correspond to the different configurations, I and II, the energy difference, ΔE=0.2 kJ mol^{-1}, was derived from the temperature dependence of the relative intensity. The activation energy (E_a) was determined by assuming that on the high temperature side of the T_{1z} minimum the dominating motion is the classical jump over the top of the barrier. For such a classical jump motion, the slope of T_{1z} on the high temperature side of the T_{1z} minimum ($\omega_0\tau_c \ll 1$) is approximately described by $E_a-2\Delta E$ (when $a \gg 1$), and more generally it is described by the relation, ln $(T_{1z}^{-1}(a+1)^3) \propto (E_a+\Delta E)/RT$. The activation energy E_a=6.9 kJ mol^{-1} was thus derived. The values, R_I=2.37 Å, R_{II}=2.16 Å, and θ=51.6°, were calculated from the structural data.[15] T_{1z} calculated by use of these parameters is shown by the broken curve in Fig. 3. Stoeckli et al. recently determined the population difference between the two configurations (I and II) for ADCA from the quasi-elastic neutron scattering experiment.[9] The ratio of the populations was 0.2:0.8 at 250 K, from which energy difference ΔE was calculated to be 2.9 kJ mol^{-1}. T_{1z} was also calculated for ΔE=2.9 kJ mol^{-1} and is shown by the dotted curve in Fig. 3.

Similar calculation of T_{1z} was performed for PNBA (Fig. 7). Because of the absence of knowledge of the structure of configuration II, we assumed $R_I=R_{II}$=2.31 Å and θ=29.5° using the available structural data.[13] The energy difference between the two configurations, ΔE=0.2 kJ mol^{-1}, was obtained from the temperature dependence of the relative intensity of the Raman bands (3080 and 3090 cm^{-1}).

The parameters used in the calculations of T_{1z} of ADCA and PNBA are listed in Table 1.

B. Quantum Mechanical Behavior of Observables of NMR Due to Proton Tunneling. The observed temperature dependences of T_{1z} of ADCA and of PNBA are obviously not explained by the classical motion as shown in Figs. 3 and 7. Especially, the small temperature coefficients of T_{1z} at low temperatures are inexplicable (1.9 kJ mol^{-1} for ADCA and 1.0 kJ mol^{-1} for PNBA). The same behavior has already been pointed out by Nagaoka et al.[6] for several other carboxylic acid dimers.

The validity or failure of the classical model can be tested in another way. Thus, the ratio T_{1z}/T_{1d} is given by[20]

$$T_{1z}/T_{1d}=2+(1/3)\,\omega_0^2\tau_c^2 \qquad (5)$$

in the case that the dipolar field is modulated by random motion and therefore T_{1z}/T_{1d} should become progressively larger as the temperature is decreased ($\omega_0\tau_c \gg 1$). The experimental results, however, showed that T_{1z}/T_{1d} is almost constant even down to such low temperatures.

The frequency dependence of T_{1z} at low temperature limit also shows (Figs. 10 and 11) a large deviation

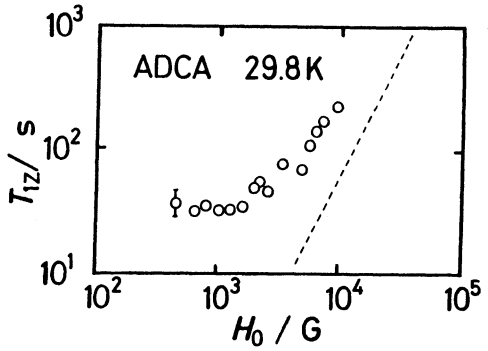

Fig. 10. Frequency (external field) dependence of spin-lattice relaxation time of Zeeman system of sublimed acetylenedicarboxylic acid.

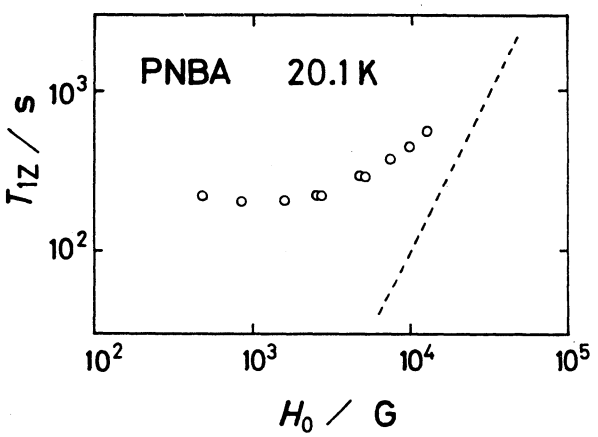

Fig. 11. Frequency (external field) dependence of spin-lattice relaxation time of Zeeman system of *p*-nitrobenzoic acid.

Table 1. Parameters of Proton Translation along the Hydrogen Bonds

	E_a/kJ mol^{-1}	ΔE/kJ mol^{-1}	τ_0/s	mCA'/s^{-2} [a]	R_I/Å	R_{II}/Å	θ/°	E_t/kJ mol^{-1}
ADCA	6.9	0.2	4.3×10^{-12}	2.45×10^{9}	2.16	2.37	51.6	1.9
	10.3	2.9[b]	3.0×10^{-12}	2.45×10^{9}	2.16	2.37	51.6	1.9
PNBA	2.5	0.2	3.7×10^{-12}	1.63×10^{8}	2.31	2.31	29.5	1.0

a) $A'=A/[a/(1+a)^2]$. b) Ref. 9.

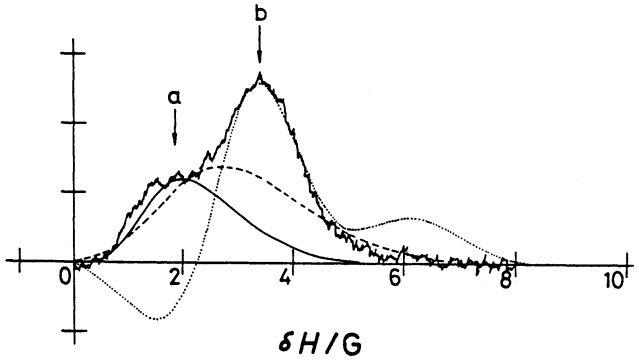

Fig. 12. A half of differential absorption line of ADCA at 4.2 K. Solid curve is the Pake doublet calculated using the parameters, proton distance r=2.37 Å and a Gaussian broadning factor β=0.8 G. Broken and dotted curves are the same calculations using the parameters r=2.16 Å (β=1.2 G) and r=1.9 Å (β=0.8 G), respectively.

from the classical prediction of H_0^2 dependence. It is obvious from this experimental result that some additional frequency terms other than the Larmor frequency must be involved in the spin relaxation formula. We can estimate that the additional frequency terms (ω') are of the order of $10^{7\pm1}$ Hz from Figs. 10 and 11. The value of H_0, at which T_{1z} begins to level off, is larger for PNBA than for ADCA. This means that ω' for PNBA is larger than for ADCA. The frequency, ω', must be connected to the tunneling rate (or tunneling frequency, ω_t) of proton translation along the hydrogen bonds.

Failure of the classical picture is also substantiated by the shape of absorption line at low temperatures (Fig. 12). It is not a simple Pake doublet[14] as one expects for an isolated proton pair like in the case of trichloroacetic acid[21] but there is another component in addition to a Pake doublet as demonstrated in Fig. 12. The peak **a** of Fig. 12 can be reproduced by the solid curve which is the Pake doublet calculated using the parameters, proton distance r=2.37 Å and a Gaussian broadning factor β=0.8 G.[14] The Pake doublet corresponding to the other configuration, r=2.16 Å (broken curve, β=1.2 G) can not explain the peak **b**. If we try to reproduce the peak **b** by a Pake doublet, we should take the parameters, r=1.9 Å and β=0.8 G (dotted curve). But there is no such a short distance between the protons. The shortest distance between the protons of different dimers of carboxyl group is 3.1 Å. Therefore the classical Pake treatment does not apply to ADCA at low temperature. The structure of the line shape disapeared, however, when the temperature was increased up to 190 K.

The more complete analysis of the line shape and its temperature dependence would require more detailed knowledge of the energy levels of the proton spin system.

Conclusion

There are two types of motions of protons in the crystals of ADCA and PNBA. The two motions are successively excited as temperature increases. At low temperatures, the protons jump between double minima along the hydrogen bond through tunneling mechanism. New evidences of proton tunneling were presented. The quantum effects are manifested not only in the temperature dependence of correlation time, τ_c, but also in the transition probability between the spin states, from which the detailed information about "tunneling" will be obtained. As the temperature is increased, the jump occurs also in the classical sense and at the same time the 180° rotation of the dimeric carboxyl group is gradually excited.

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