Temperature Dependence of ^{2}H Nuclear Quadrupole Interaction in Very Short Hydrogen Bonds in Some Organic Acidic Salt Crystals

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The ^{2}H nuclear quadrupole interaction parameters, e^2Qq/h and η, are closely related to the shape of the potential energy surface at hydrogen bonds and depend sensitively on their geometry. We measured the temperature dependence of the ^{2}H NMR spectra of the crystalline acidic salts $KDCO_3$, KD acetylenedicarboxylate, RbD acetylenedicarboxylate, and KD maleate, which contain very short O-D···O type hydrogen bonds. The temperature coefficient decreases with increase in the O···O distance in the hydrogen bond. *Ab inito* molecular orbital calculations of the electric field gradient tensor based on the temperature dependent structure of each crystal indicate that thermal expansion of the hydrogen bond geometry is not responsible for this tendency. *Ab initio* calculations also predict that a fictitious off center shift of the hydrogen position in a symmetric hydrogen bond causes very high e^2Qq/h values. This suggests that low energy vibrational excitation may be responsible for large positive $\mathrm{d}(e^2Qq/h)/\mathrm{d}T$ values in symmetric hydrogen bonds.

Key words: Hydrogen Bond; Quadrupole Coupling Constant; ^{2}H NMR.

1. Introduction

Very often hydrogen bonds play an essential role in crystal chemistry and physics, secondary structure and functions of biological systems such as peptides and proteins, phase transitions in crystalline materials, the appearance of the ferroelectricity, *etc*. Various kinds of experimental studies have been executed and a great number of theoretical models have been proposed to interpret various phenomena concerning hydrogen bonds. However, many difficult problems still remain, especially as to the temperature dependence of the structure and dynamic properties of so-called very short hydrogen bonding systems. Usually many properties of hydrogen bonds, including dynamic properties, *i. e.*, the excitation of motion of the hydrogen, have been discussed on the basis of a rigid and temperature independent potential energy surface. For very short hydrogen bonds, however, it is anticipated that the shape of the potential energy surface varies with the hydrogen bond length *e. g.*, from a double-minimum potential to a single-minimum one [1]. In such a case the simple assumption of a rigid potential surface often fails to describe various phenomena characteristic for very short hydrogen bonds.

The ^{2}H quadrupole coupling constant (e^2Qq/h) for the hydrogen or deuterium involved in a hydrogen bond can be a very sensitive probe to characterize the hydrogen bond. The correlation between the deuteron quadrupole coupling constant and the hydrogen bond geometry, for example the O-H···O hydrogen bond distance $R_{\mathrm{O\cdots O}}$, has long been used to discuss the structure and the properties of hydrogen bonds [2 - 5]. In Fig. 1 we have reproduced the correlation diagram using the data collected in [4, 5] and in this work. In the short hydrogen bond region, where $R_{\mathrm{O\cdots O}}$ becomes smaller than 0.26 nm, the slope of e^2Qq/h becomes steeper, but the scattering of the numerical values of η becomes larger, suggesting that the shape of the potential function can change in various manners in the short hydrogen bond region. Kalsbeek *et al.* observed that there are two types of temperature dependences of the quadrupole interaction

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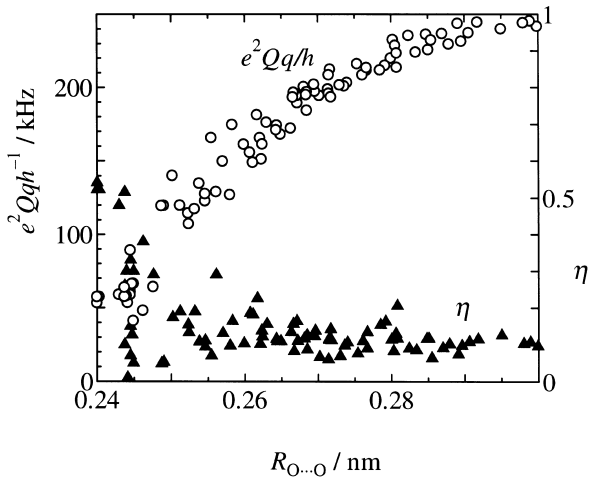

Fig. 1. The correlation between e^2Qq/h (open circles) and η (closed triangles) of ^{2}H and the O···O hydrogen bond length (after [4]).

parameters in short hydrogen bonds of acid salts [6]. An asymmetric hydrogen bond gives an e^2Qq/h that decreases with increase in temperature, whereas a symmetric hydrogen bond has a e^2Qq/h which increases with temperature. The former is widely seen in many molecular and ionic crystals [7]. From *ab initio* molecular orbital calculations of e^2Qq/h for model systems it was guessed that the temperature dependence of e^2Qq/h can be interpreted by a vibrational effect. However the vibrational excitation energy is too high or the corresponding increase in e^2Qq/h is too small. Therefore further research is needed for understanding the temperature dependence of the ^{2}H nuclear quadrupole interaction in *short* hydrogen bonds.

We now measured the temperature dependence of ^{2}H NMR spectra of deuterons in the very short O-H···O type hydrogen bonds appearing in some crystalline acidic salts. To extract any essential factor or factors that govern the temperature dependence of e^2Qq/h, we also carried out *ab initio* molecular orbital theoretical calculations based on actual crystalline structure.

2. Experimental

$KHCO_3$ was supplied from WAKO Chemicals. Potassium hydrogen maleate and potassium hydrogen acetylenedicarboxylate were crystallized by evaporation of aqueous solutions of stoichiometric mixture of KOH and maleic acid (Nacalai Tesque) or acetylenedicarboxylic acid (Tokyo Kasei Inc.), respectively. Rubidium hydrogen acetylendicarboxylate was prepared from an aqueous solution of $RbCO_3$ and acetylenedicarboxylic acid. All deuterated specimens were recrystallized from D_2O (CIL 99.9% ^{2}H concentration) solutions under air-free condition.

^{2}H NMR was observed using Bruker MSL-200 and/or DSX-200 spectrometers at 30.7 MHz. Each sample was grinded to powder and sealed in a glass ampoule with a small amount of He gas for heat exchange. To observe a ^{2}H NMR spectrum, 64-2048 FIDs were accumulated using quadrupole-echo pulse sequences with 90° pulse length of 4 μs and pulse distance of 15 μs. e^2Qq/h and η were determined by using spectrum simulation.

Ab initio molecular orbital calculations of the electric field gradient (EFG) tensor components at the hydrogen position in the crystal were performed by the CRYSTAL95 program package [8] with STO-3G basis set adapting the actual crystal structure data determined by neutron or X-ray diffraction experiments. Calculated EFG values in a. u. were converted to e^2Qq/h in kHz by multiplying with a scaling factor of 555.6 kHz/a.u. deduced in [9]. Because this conversion factor includes some ambiguity, hereafter we will deal only with relative values of e^2Qq/h.

3. Results of ^{2}H NMR Experiments

3.1. Potassium Hydrogen Maleate

Crystalline potassium hydrogen maleate belongs to the orthorhombic *Pbcm* space group [10, 11]. A maleate anion forms a 7-member ring by intramolecular hydrogen bonds between two carboxyl groups. The hydrogen maleate anion has mirror symmetry perpendicular to the molecular plane. The intramolecular O-H···O type hydrogen bond is very short ($R_{O\cdots O}$ = 0.2427 nm) and symmetric. ^{2}H NMR studies at room temperature have been carried by several researchers [2, 12], which report that e^2Qq/h = (56.0 ± 0.8) kHz and η = 0.53 ± 0.07 [2], e^2Qq/h = (57.2 ± 0.5) kHz and η = 0.516 ± 0.02 (291 K) [12]. We measured the ^{2}H NMR spectrum at various temperatures as shown in Figure 2. The line width increases significantly with increase in temperature, implying that e^2Qq/h increases with increase in temperature. On the other hand, the line shape of the ^{2}H NMR spectrum is

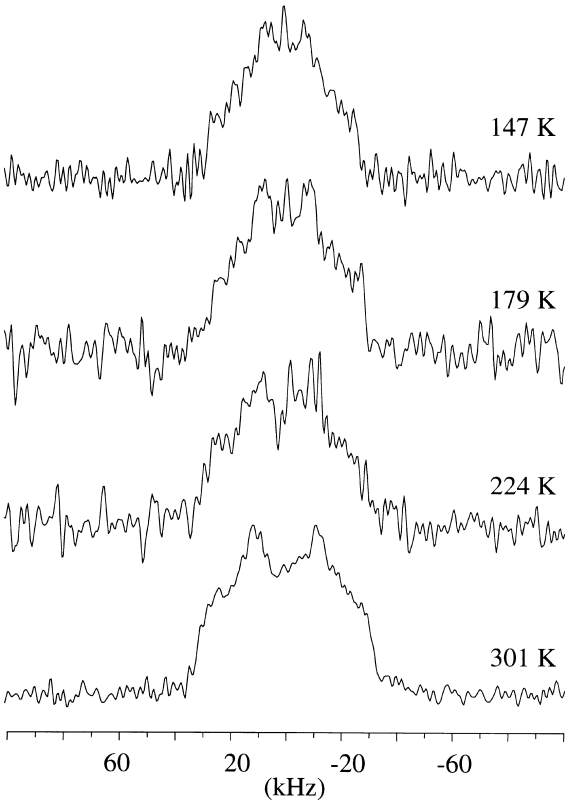

Fig. 2. Temperature dependence of the ^{2}H NMR spectrum of KH maleate.

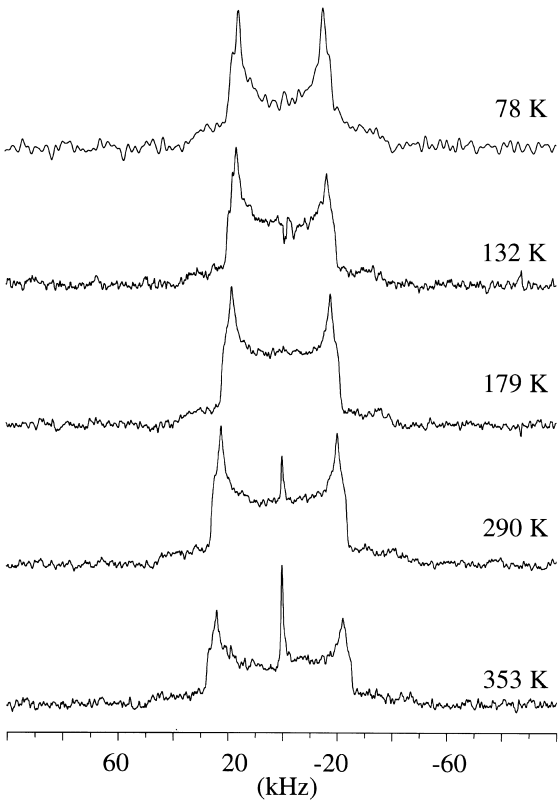

Fig. 3. Temperature dependence of the ^{2}H NMR spectrum of KH acetylenedicarboxylate.

almost unchanged over the whole temperature range, indicating that η is rather independent of temperature.

3.2. Potassium and Rubidium Hydrogen Acetylenedicarboxylate

KH acetylenedicarboxylate and RbH acetylenedicarboxylate are isomorphous and crystallize in a monoclinic unit cell with the space group *C*2/*c* [13, 14]. Acetylenedicarboxylate anions form one-dimensional chains linked by very short hydrogen bonds ($R_{O\cdots O}$ is 0.2445 nm for the K-salt [13] and 0.2449 nm for the Rb-salt [14]), each chain being symmetric and identified by the two-fold rotation axis through the center of the hydrogen bond. The temperature dependence of the ^{2}H NMR spectrum of the K-salt is shown in Figure 3. The sharp peak at the center of the spectrum at high temperatures is due to a trace of solvent D_2O. The spectral line shape does not undergo any significant change on heating, but the line width increases remarkably with increasing in temperature. The ^{2}H NMR spectrum of the Rb-salt has a similar temperature dependence, though e^2Qq/h of the K-salt is considerably smaller than that of the Rb-salt; this difference may originate from the difference in $R_{O\cdots O}$ in these salts. η is nearly equal to 0.1 for both salts.

3.3. Potassium Hydrogen Carbonate

Potassium hydrogen carbonate crystallizes in a monoclinic unit cell with the space group $P2_1/a$ [15, 16]. Two carbonate anions couple via a pair of hydrogen bonds to form a dimeric unit. A neutron diffraction study revealed that each of these hydrogen bonds belongs to a typical asymmetric double minimum hydrogen bond [16]. Single crystal ^{2}H NMR experiments [2, 17] and a ^{2}H-^{1}H double resonance study [18] were carried out at room temperature, resulting in e^2Qq/h = 154 kHz η = 0.19. The measurements of the spin-lattice relaxation time, T_1, of ^{2}H did show

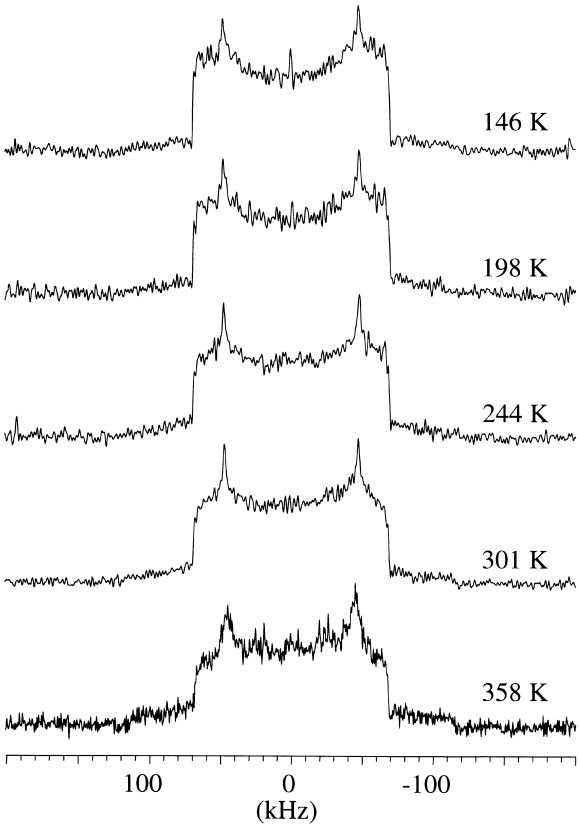

Fig. 4. Temperature dependence of the ^{2}H NMR spectrum of $KDCO_3$.

that the chemical exchange of the acidic proton or deuterium in the asymmetric hydrogen bond potential takes place [19]. The temperature dependence of the powder ^{2}H spectrum measured in the present work is shown in Figure 4. It shows that no significant variation of the spectrum occurs in the temperature range of the measurements. Indeed, the analyses of the spectrum confirmed that both e^2Qq/h and η have weak temperature dependences in comparison with those for other salts. It is noted that e^2Qq/h has a small and *negative* temperature coefficient.

4. Discussion

The temperature dependence of e^2Qq/h and η for all materials is plotted in Figure 5. η is almost independent of temperature for all substances. On the other hand, e^2Qq/h increases linearly with temperature for KH maleate, KH acetylenedicarboxylate, and RbH acetylenedicarboxylate. For $KHCO_3$ e^2Qq/h decreases slightly with temperature. Estimated $\mathrm{d}\,(e^2Qq/h)/\mathrm{d}\,T$ values are summarized in Table 1 together with the data estimated by referring to the figures in [6]. Roughly speaking, the shorter the hydrogen bond has the larger $\mathrm{d}\,(e^2Qq/h)/\mathrm{d}\,T$.

Table 1. Observed e^2Qq/h and η at room temperature, and $\mathrm{d}\,(e^2Qq/h)/\mathrm{d}\,T$ of acidic salts.

Substance	$R_{\mathrm{O}\cdots\mathrm{O}}$ mm	e^2Qq/h kHz	η	$\mathrm{d}(e^2Qq/h)/\mathrm{d}\,T$ kHz K^{-1}	Ref.
KH maleate	0.2437	57.2	0.52	10.1×10^{-2}	*
KH succinate	0.24413	53.3	0.01	6.2×10^{-2}	[6]
$MeNH_3$ succinate·H_2O	0.24448	58.6	0.15	7.5×10^{-2}	[6]
KH acetylene-dicarboxylate	0.2445	60.5	0.07	7.8×10^{-2}	*
RbH acetylene-dicarboxylate	0.2449	66.1	0.05	7.8×10^{-2}	*
NaH malonate	0.25546	165.5	0.07	-3.5×10^{-2}	[6]
$KHCO_3$	0.2607	154.5	0.19	-2×10^{-2}	*

* This work.

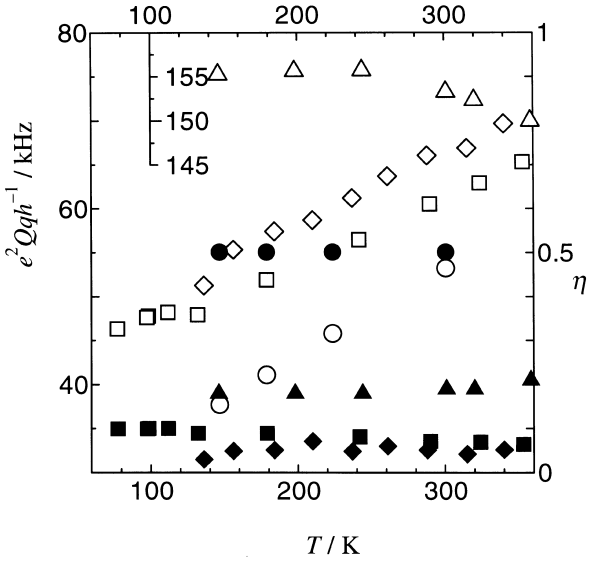

Fig. 5. Temperature dependence of e^2Qq/h (open symbols) and η (closed symbols) of acidic salts. KH maleate: circles; KH acetylenedicarboxylate: squares; RbH acetylenedicarboxylate: diamonds; KH carbonate: triangles. e^2Qq/h of $KHCO_3$ uses another scale in the plot area.

Results of *ab initio* molecular orbital calculations for crystals are shown in Table 2. The calculated e^2Qq/h for $KHCO_3$ does not show a regular dependence on temperature; this results probably from the irregular variation of the hydrogen bond length $R_{\mathrm{O}\cdots\mathrm{O}}$ as listed in Table 2. Perhaps some defect has happened

Table 2. Results of the calculation of e^2Qq/h and η by using the CRYSTAL95 program package based on the actual crystal structure at various temperatures, and also on fictitious hydrogen displaced structures of KH maleate. ΔE is the difference between the total energy in the actual crystal and that in the fictitious structure.

Substance	$R_{O...O}$ mm	Ref.	e^2Qq/h kHz	η	ΔE kHz K^{-1}	Condition**
KH maleate	0.2427	[10]	18.7	0.90		5 K
		[10]	18.7	0.90		14 K
	0.2437	[10]	18.9	0.91	0*	300 K
			18.7	0.92	19.4	0.010 nm s
			70.0	0.32	63.3	0.015 nm s
			132.7	0.46	122.0	0.020 nm s
			17.8	0.79	7.8	0.005 nm b
			17.5	0.76	15.1	0.010 nm b
KH acetylene-dicarboxylate	0.2445	[12]	24.4	0.48		
RbH acetylene-dicarboxylate	0.2449	[13]	25.8	0.18		
$KDCO_3$	0.2606	[14]	263.7	0.11		95 K
	0.2613	[14]	287.7	0.11		219 K
	0.2607	[14]	236.4	0.12		298 K

* Taken as standard. ** s: displace hydrogen along O-H direction; b: displace hydrogen along O-H-O bending direction.

in the diffraction experiments on this compound. We therefore cannot use the present computational results to evaluate the small but negative temperature coefficient of the e^2Qq/h in this substance.

The calculated quadrupole interaction parameters for KH maleate at different temperatures indicate that e^2Qq/h as well as η are constant over whole temperature range. This implies that the structure of the *intramolecular* hydrogen bond is not affected by the thermal expansion of the crystal lattice. We must look for the cause of the large positive temperature coefficient of e^2Qq/h in this compound together with those for KH- and RbH-acetylenedicarboxylates, which are typical intermolecular hydrogen bonding systems.

Kalsbeek *et al.* considered that excitation of the vibrational stretching mode causes the increase of e^2Qq/h if the hydrogen bond is very short [6]. They estimated by their calculations on model molecules that e^2Qq/h increases by about 20 kHz if a displacement of H or D by 0.02 nm takes place. Since the ratio of the number of H's in the first vibrational excited state, which is by 1000 cm^{-1} higher than the ground state, to the number of H in the ground state is about 0.01 at 300 K, the vibrational stretching leads to a negligibly small change in the e^2Qq/h, and therefore the vibrational effect cannot account for the observed large positive temperature coefficient of e^2Qq/h.

The INDO semi-empirical SCF calculations by Žaucer *et al.* resulted in considerable increase of e^2Qq/h for the hydrogen-displaced maleate anion [20]. To confirm this point we carried out *ab initio* molecular orbital calculations based on the fictitious hydrogen-displaced structure of KH maleate. First of all, the hydrogen was shifted from the central position along the O···O axis by a suitable amount, and the corresponding EFG together with the total energy of the crystal were calculated. The results are shown in Table 2. e^2Qq/h increases sharply when the displacement of the hydrogen is larger than 0.01 nm. However, since the total crystal energy becomes as high as 122 kJ mol^{-1} for a displacement of 0.02 nm, the displacement of the hydrogen accompanied by the vibrational excitation should be restricted to a very small amplitude, and so we cannot expect a sufficient increase of the EFG by the vibrational excitation.

Recent inelastic neutron scattering (INS) experiments pointed out the existence of low energy bands near 500 cm^{-1} above the ground state in relation to the OHO asymmetric stretching [11]; this energy relation allows the occupation of excited state by 8%, and in the case of such a low energy excitation, the above mechanism may work. For a more quantitative estimation, more detailed calculations concerning the vibrational excited states and experiments at lower temperatures would be required.

When the hydrogen position is displaced perpendicular to the O···O bond, the variation of both e^2Qq/h and the total energy is small. This suggests that the direct contribution of bending excitation state to e^2Qq/h is negligible. Perhaps only the Bayer type vibrational averaging effect works in the case of the bending vibration [7]. In order to understand the large positive and also sometimes negative temperature coefficient of the quadrupole coupling constant for hydrogen bonded systems in various materials, it may be necessary to introduce a dynamical coupling between the hydrogen bonds which would lead to a kind of collective excitation of hydrogen bonded networks.

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