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Deuteron Quadrupole Interactions in Two Modifications of Oxalic Acid Dihydrate Crystal

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A brief account has been previously published of the deuteron quadrupole interactions in the α and β modifications of the deuterated oxalic acid dihydrate crystal, $C_2O_4D_2 \cdot 2D_2O$, in relation to their structures.[1] In this note, the details of the results of deuteron magnetic resonance and a discussion with reference to the structures, as determined by recent extensive diffraction studies,[2] will be given.

As is to be expected from the similarities in their structures, the deuteron resonance spectra of the α-form have features similar to those of the β-form, which have been measured previously.[3] The water deuterons showed spectra characteristic of a 180°-flip motion of D_2O: lines of stationary deuterons at low temperatures, fast-motion-averaged lines at high temperatures, and broadened-out lines in the intermediate temperature range. The values of the deuteron quadrupole coupling (eqQ/h), the asymmetry parameter (η), and the direction cosines of the principal axes of the field gradient tensors are listed in Table 1[4] ($|q_{zz}| \geq |q_{yy}| \geq q_{xx}|$ assumed). The values listed for the β-form are those revised by the computor processing[5] of the previous experimental results[3] by including some additional new data.

The two empirical relations[1,5] that 1) the z principal axis is in the bond direction, and that 2) the y principal axis is perpendicular to the plane formed by the D–X–Y, are examined. In view of the structure determined by the neutron diffraction studies,[2] as is shown in Table 2, the deviation angles from these relations, θ_z and θ_y, are within the range usually found, namely, $\theta_z \lesssim 3°$ and $\theta_y \lesssim 10°$, providing other evidence of the usefulness of determining bond directions from the deuteron resonance.

The eqQ *vs.* $r(O \cdots O)$ (the hydrogen bond length)-plot generally fits well to the smooth curve relation

TABLE 1. DEUTERON QUADRUPOLE COUPLING eqQ/h, ASYMMETRY PARAMETER, η, AND THE DIRECTION COSINES OF z AND y PRINCIPAL AXES IN α- AND β-FORM $C_2O_4D_2 \cdot 2D_2O$ CRYSTALS

	Temperature (°C)	eqQ/h (kHz)	η (%)				
α-Form					a	b	c^*
D_1^α	−82	107.1±0.5	13.3±0.5	z	−0.587	±0.247	0.771
	25	118.0±1.1	11.3±1.1	y	0.399	±0.917	0.010
D_2^α	−82	229.4±1.8	10.2±1.0	z	0.563	±0.266	0.783
				y	−0.603	±0.780	0.169
D_3^α	−82	237.2±0.7	10.8±0.4	z	0.699	±0.650	−0.300
				y	−0.620	±0.759	0.200
D_2^α, D_3^α (Motion-averaged)	25	125.6±1.3	89.0±1.9	z	−0.633	±0.759	0.153
				y	0.766	±0.584	0.268
β-Form					a^*	b	c
D_1^β	−70	134.7±0.5	10.8±0.6	z	−0.655	∓0.152	0.740
	25	139.1±0.3	9.3±0.5	y	0.581	±0.524	0.623
	67	140.4±0.4	10.2±0.5				
D_2^β	−70	232.2±1.0	6.4±0.5	z	−0.171	∓0.497	0.851
				y	0.615	±0.621	0.486
D_3^β	−70	223.9±0.8	8.5±0.5	z	−0.668	±0.729	−0.150
				y	0.589	±0.642	0.491
D_2^β, D_3^β (Motion-averaged)	67	120.5±0.4	92.8±0.6	z	−0.286	±0.732	−0.619
				y	0.543	±0.656	0.525

Principal directions for D_1's listed are the room temperature values. The values at other temperatures are substantially unchanged.

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[1] T. Chiba and G. Soda, "Magnetic Resonance and Relaxation," Proc. 14th Colloque Ampère, Ljubljana, North-Holland Publ. Co., Amsterdam (1966), p. 722.

[2] R. G. Delaplane and J. A. Ibers, *Acta Crystallogr.* **B25**, 2423 (1969); P. Coppens and T. M. Sabine, *ibid.*, 2442 (1969).

[3] T. Chiba, *J. Chem. Phys.*, **41**, 1352 (1964).

[4] The hydrogen atoms are differently numbered by various authors. In this note we adopt the numbering of Ref. 2: D_1 (acid), D_2 (water) incorporated in the *ac*-plane hydrogen-bond network, and D_3 (water) incorporated in the screw hydrogen-bond network in the *b*-axis direction. The crystal form is indicated by a superfix, α or β.

[5] G. Soda and T. Chiba, *J. Chem. Phys.*, **50**, 439 (1969).

TABLE 2. DEVIATION ANGLES OF THE z PRINCIPAL AXES FROM THE O-D DIRECTION, θ_z, AND THOSE OF THE y PRINCIPAL AXES FROM THE COD OR D_2O PLANE NORMALS, θ_y

	D_1^α	D_2^α	D_3^α	D_1^β	D_2^β	D_3^β
θ_z	0.9°	2.8°	1.4°	1.0°	3.0°	1.5°
θ_y	8.9°	2.0°	1.7°	4.3°	4.4°	2.7°

previously presented (Fig. 1).[3,5,6] Small systematic deviations for the water deuterons need to be mentioned, however. The D_3^α and D_2^β points above the curve of the *eqQ vs.* r(O···O)-plot are from bent hydrogen bonds (156° and 157°), while the D_2^α and D_3^β points are from nearly straight hydrogen bonds (168° and 170°). The fitting to a smooth curve is perfect if *eqQ* is plotted against r(O···O), as in Fig. 1. This seems reasonable because, in a weak hydrogen bond, the strength of the bond must primarily be determined by the electrostatic interaction between the H and the hydrogen-bond-acceptor atom. This is also consistent with the good correlation of *eqQ*-r(O···D) as given in the form of an empirical equation.[5] The O–D distance, which reflects the hydrogen bond strength, should have primary importance in determining the *eqQ*. The correlation between *eqQ* and r(O–D) is, however, not very satisfactory (Fig. 1), (see also Fig. 5 of Ref. 7).

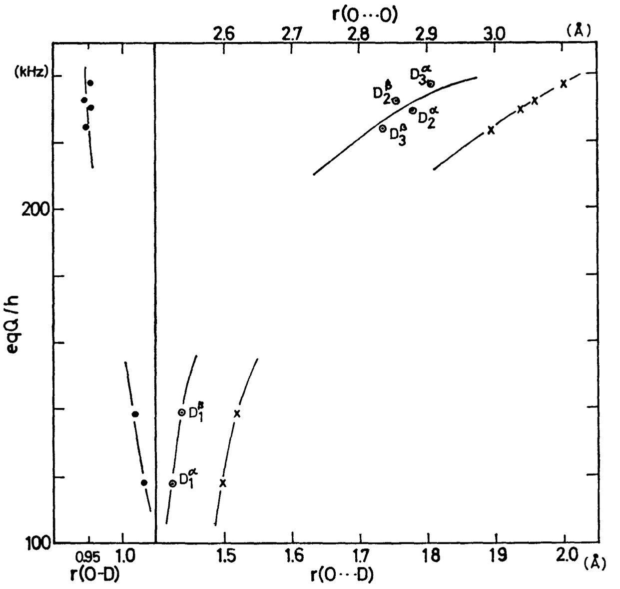

Fig. 1. Deuteron quadrupole coupling values in α- and β-$C_2O_4D_2 \cdot 2D_2O$ plotted against r(O...O) (⊙), r(O...D) (×), and r(O–D) (●).

The dependence of the *eqQ* on the r(O···O) or on r(O···D) is so apparent that it seems reasonable to ascribe the origin of the marked positive temperature dependence of the *eqQ* of the D_1^α to the temperature variation of the r(O···O) or r(O···D). If the r(O···O) dependence of *eqQ* is estimated from a comparison of the D_1^α and D_1^β data at room temperature, an increase in the *eqQ* of D_1^α from 107.1 kHz at 191°K to 118.0 kHz at 298°K must be caused by the 0.008 Å increase in the r(O···O). The maximum thermal expansion in the *ac* plane of the α-form crystal is reported to be in the direction nearly parallel to the O–D_1···O and O–D_3···O, with a coefficient of 0.0114 for a 90—290°K change.[8] This amounts to a lengthening of 0.079 Å for each pair of O–D_1···O and O–D_3···O bonds if we assume this expansion to be shared by these two hydrogen-bond systems. Actually, the expansion is accompanied by the deformation of various parts, and the fraction shared by the O–D_1···O bond is not known, but the increase in the O–D_1···O length by 0.008 Å from 191° to 298°K is small enough to be well explained by the thermal expansion.

The large amplitudes of a torsional oscillation approximately perpendicular to the plane of the oxalic acid molecule and a translational oscillation about the axis approximately parallel to the C–C bond were concluded to exist in these crystals from the large thermal parameters observed in the structure analyses.[2] This may be another possible cause of the positive temperature dependence of *eqQ*. These oscillations force the OD_1 group to oscillate in the direction perpendicular to the O–D_1···O bond, thus tending to increase the average D_1···O separation. The total mean-square amplitude at room temperature of these two oscillations for the OD_1 group is 0.060 Å^2 ((0.24 Å)^2). As a rough estimate, if these oscillation frequencies are assumed to be less than 50 cm^{-1}, a decrease in the average D···O distance by more than 0.0067 Å can be expected for a 298° to 191° K change. The assumed frequency range may not be unreasonable for the type of oscillations considered here, and this mechanism can explain most of the required change in the D···O distance. Other effects, such as the bending vibration of the OD bond, which lead to a (normal) negative temperature variation of the *eqQ* may also be present, and the observed temperature dependence of *eqQ* is actually a sum of various contributions.

A similar but smaller positive temperature dependence of *eqQ* for acid deuteron is observed for the β-form crystal (5.7 kHz for −70°—67°C) and in potassium binoxalate, KDC_2O_4 (6.1 kHz for −37.3°—137.7°C).[7] These phenomena may also be due to the mechanisms of the types considered above. For deuterons in weaker hydrogen bonds, the lengthening of the hydrogen-bond distance by thermal expansion or by oscillation makes a smaller contribution to the temperature dependence of *eqQ*. This is probably the reason why temperature dependence of the *eqQ* of water deuterons can often be well explained by the simple Bayer theory.[9,10]

A change in the strength of the O–D···O bond indicated by the positive temperature dependence of *eqQ* would imply a decrease in the OH vibration frequency with the temperature. In this respect, the

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6) The correlation of the *eqQ* values of water deuterons for reduction by a torsional motion, as in Fig. 5 of Ref. 3, is not made.

7) J. W. McGrath, *J. Chem. Phys.*, **48**, 5549 (1968).

8) J. M. Robertson and A. R. Ubbelohde, *Proc. Roy. Soc.*, **A170**, 241 (1939).

9) H. Bayer, *Z. Physik.*, **130**, 227 (1951).

10) T. Chiba, *J. Chem. Phys.*, **39**, 947 (1963); T. Chiba and G. Soda, This Bulletin, **41**, 1524 (1968).

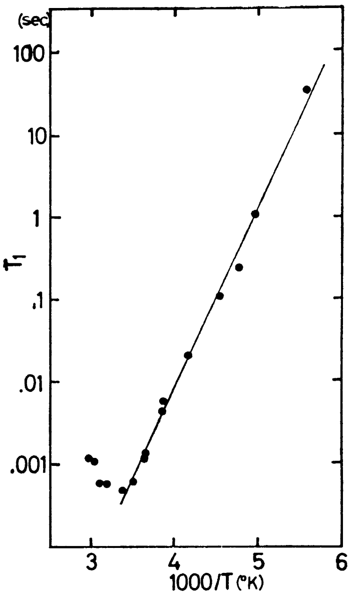

Fig. 2. Temperature dependence of T_1 of water deuterons in α-form $C_2O_4D_2 \cdot 2D_2O$.

temperature dependence of the vibration spectra in these crystals is of interest.

Because data on the line-width change with the temperature in the α-form crystal were rather poor, we estimated the barrier height of the flip motion of the D_2O to be 9.7 kcal/mol from the temperature dependence of the spin-lattice relaxation time, T_1 (Fig. 2.) This value is less than 10.7 kcal/mol (a revised value of the previous measurement[3,11]) for the β-form; this is consistent with the fact[5] that the hydrogen bonds linking the water molecule are slightly longer in the α-form than in the β-form.

Experimental

The α-form $C_2O_4D_2 \cdot 2D_2O$ crystals were grown from a saturated solution, whose deuterium content was controlled to about 90%, by gradual cooling. The angular dependence of the quadrupole splittings when the magnetic field was rotated about the *a*, *b*, and c^* axes was measured at various temperatures; the quadrupole coupling tensors were then determined by the method described previously.[5] The T_1 of D was measured by the pulse method using the 180°—90° pulse sequences at 10 MHz.[11] The magnetic field was applied in a direction (nearly parallel to the *c* axis) on the *ac* plane where quadrupole splittings of the water deuterons are sufficiently small to give a single-valued T_1. In this setting, D_1 lines are about 40 kHz apart and need not be considered.

The measurement of the deuteron resonance and the computor analysis of the data were done at the Institute for Solid State Physics, The University of Tokyo. We wish to thank Professor Y. Kakiuchi of the Institute for his interest in this work and for providing the facilities. We also wish to thank Messrs. A. Suetaka and T. Kataoka for their assistance in the experiment.

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[11] T. Chiba and Y. Kakiuchi, This Bulletin, **41**, 828 (1968).