

Hydration Structure around the Carbonyl Group of an Urea Molecule in Concentrated Aqueous Solutions Studied by Neutron Diffraction with $^{12}C/^{13}C$ Isotopic Substitution

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Neutron diffraction measurements were carried out at 25 °C on aqueous 15 mol % urea heavy water solutions, $[(ND_2)_2{}^*C{=}O]_{0.15}(D_2O)_{0.85}$, in which the $^{12}C/^{13}C$ isotopic composition of the carbonyl-carbon atom was changed. The hydration structure around the carbonyl-carbon atom was derived from the least-squares fitting analysis of the observed first-order difference function, $\Delta_C(Q)$. From the analysis, 4.3(3) water molecules are hydrogen-bonded to the carbonyl-oxygen atom with the intermolecular $C\cdots D_{W1}$ (D_{W1}: water deuterium atom) distance of 2.46(3) Å. The average angle, $\angle C\cdots D_{W1}{-}O_W$ (O_W: water oxygen atom), was determined to be 124(5)°.

The hydration structure of the urea molecule has received much attention because of its importance for various fields of chemical and biological sciences. From an X-ray diffraction study by Adams et al., the hydrogen-bonded network among the water molecules is distorted in highly concentrated aqueous urea solutions.[1] Recent molecular dynamics (MD) simulations on aqueous urea solutions have shown that the bulk water structure is retained beyond the first hydration shell of the urea molecule.[2–6] The H–H and H–X (X: O, C, and N) partial distribution functions derived from the neutron diffraction measurements with H/D isotopic substituted aqueous 10 m (15.3 mol %) urea solutions indicated a shift in the average hydrogen-bonded distances compared to pure water.[7] The hydration structure around the amino group of the urea molecule was investigated by means of the neutron diffraction with $^{14}N/^{15}N$ isotopic substitution method.[8–14] The average number of water molecules that are hydrogen-bonded per one amino group was 2.0(1) with the nearest neighbor $N\cdots O_W$ and $N\cdots H_W$ distances of 2.92(1) and 3.42(1) Å, respectively.[13] Soper et al. have reported the results of neutron diffraction measurements on five highly concentrated aqueous 20 mol % urea solutions with different H/D and $^{14}N/^{15}N$ ratios.[14] Results of the EPSR analysis indicated that the urea molecules form pronounced hydrogen bonds with the neighboring water molecules at both the amino and carbonyl groups.[14] In order to determine the hydration structure around the carbonyl group of the urea molecule, it is necessary to obtain direct information on structural parameters of intermolecular interaction between the carbonyl group and the neighboring water molecules. Neutron diffraction with $^{12}C/^{13}C$ isotopic substitution is considered to be one of the most suitable experimental techniques, and an early attempt to apply $^{12}C/^{13}C$ isotopic substitution to the liquid methanol has shown the feasibility of this technique to investigate the structure of liquids and solutions.[11] Recently, $^{12}C/^{13}C$ isotopic substitution was used to determine the hydration structure around the carboxyl group of the acetate ion.[15]

In this paper, we describe results of neutron diffraction measurements on concentrated aqueous 15 mol % urea heavy water solutions with different $^{12}C/^{13}C$ isotopic compositions. The difference function, $\Delta_C(Q)$, from the two solutions with different $^{12}C/^{13}C$ ratio, $[(ND_2)_2{}^{nat}C{=}O]_{0.15}(D_2O)_{0.85}$ (^{nat}C: natural abundance) and $[(ND_2)_2{}^{13}C{=}O]_{0.15}(D_2O)_{0.85}$, gives direct information concerning the distribution of water molecules around the carbonyl-carbon atom.

Experimental

Materials. Isotopically enriched $(NH_2)_2{}^{13}C{=}O$ (99% ^{13}C, manufacturer's specification, Aldrich Chemical Co., Inc.) and natural $(NH_2)_2{}^{nat}C{=}O$ (98.9% ^{12}C, natural abundance, Nacalai Tesque, guaranteed grade) were deuterated by dissolving them into 10 times the molar quantity of D_2O (99.9% D, Aldrich Chemical Co., Inc.), followed by dehydration under the vacuum. This procedure was repeated 4 times. The required amounts of enriched compounds, $(ND_2)_2{}^{13}C{=}O$ and $(ND_2)_2{}^{nat}C{=}O$, were dissolved into D_2O (99.9% D, Aldrich Chemical Co., Inc.) to prepare two aqueous 15 mol % urea solutions with different $^{12}C/^{13}C$ isotopic composition, $[(ND_2)_2{}^{nat}C{=}O]_{0.15}(D_2O)_{0.85}$ (I) and $[(ND_2)_2{}^{13}C{=}O]_{0.15}(D_2O)_{0.85}$ (II).

The H/D isotopic ratio of the exchangeable hydrogen atoms within the D_2O solutions was carefully determined through measurements for the integral absorption intensity of the O–H stretching vibrational band using a JASCO FT/IR-410 spectrometer with the ATR attachment (ATR-500/M with a Ge prism). The D content of the exchangeable hydrogen atoms was estimated to be $99.9 \pm 0.1\%$. The ^{13}C content in anhydrous $(NH_2)_2{}^{13}C{=}O$ was determined to be $99.5 \pm 0.2\%$ using the JASCO EX-130S ^{13}C analyzer. Each sample solution was sealed in a cylindrical fused quartz cell (11.6 mm in inner diameter and 1.2 mm in thickness) and used for neutron diffraction measurements. The sample parameters used in the present study are listed in Table 1.

Neutron Diffraction Measurements. Neutron diffraction measurements were carried out at 25 °C using an ISSP 4G (GPTAS) diffractometer installed at the JRR-3M research reactor

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Table 1. Isotopic Composition, Mean Scattering Length, b_C, of the Carbon Atom, Total Cross Sections, and Number Density of Sample Solutions in the Stoichiometric Unit, $[(ND_2)_2{}^*C{=}O]_{0.15}(D_2O)_{0.85}$, σ_t, and ρ, Respectively

Sample		$^{12}C/\%$	$^{13}C/\%$	$b_C/10^{-12}$ cm	σ_t/barns[a)]	$\rho/\text{Å}^{-3}$
I	$[(ND_2)_2{}^{nat}C{=}O]_{0.15}(D_2O)_{0.85}$	98.9	1.1	0.6646	16.610	0.02719
II	$[(ND_2)_2{}^{13}C{=}O]_{0.15}(D_2O)_{0.85}$	0.5	99.5	0.6192	16.488	

a) For incident neutron wavelength of 1.062 Å.

operated at 20 MW in the Japan Atomic Energy Research Institute (JAERI), Tokai, Japan. The incident neutron wavelength, $\lambda = 1.062 \pm 0.004$ Å, was determined by Bragg reflections from KCl powder. Beam collimations used were 40′–80′–80′ in going from the reactor to the detector. The aperture of the collimated incident beam was 15 mm in width and 40 mm in height. Scattered neutrons were collected over the angular range of $3.0 \leq 2\theta \leq 118°$, which corresponds to the scattering vector magnitude of $0.31 \leq Q \leq 10.14$ Å^{-1} ($Q = 4\pi \sin\theta/\lambda$). The angular step interval was chosen to be $\Delta(2\theta) = 0.5°$ in the range of $3 \leq 2\theta \leq 40°$ and $\Delta(2\theta) = 1°$ in the range of $41 \leq 2\theta \leq 118°$, respectively. The preset time was set to 400 s. The total number of observed counts was at least 2.5×10^5 counts, and ranged as high as 5.3×10^5 counts. Scattering intensities were measured in advance for a vanadium rod (10 mm in diameter), empty cell, and background, respectively.

Data Reduction. Observed scattering intensities from the sample were corrected for instrumental background, absorption,[16] and multiple scattering.[17] The observed count rate for the sample solution was converted to the absolute scale by the use of corrected scattering intensities from the vanadium rod. Details of the data correction and normalization procedures have been described in previous reports.[18,19]

The first-order difference function,[20–22] $\Delta_C(Q)$, was obtained as the numerical difference of normalized scattering cross section from sample solutions, that are identical except for the isotopic composition of the carbonyl-carbon atom within the urea molecule:

$$\Delta_C(Q) = (d\sigma/d\Omega)^{obs}(\text{for sample I}) - (d\sigma/d\Omega)^{obs}(\text{for sample II}). \quad (1)$$

The $\Delta_C(Q)$, scaled at the stoichiometric unit, $[(ND_2)_2{}^*C{=}O]_x(D_2O)_{1-x}$, is expressed as the weighted sum of four partial structure factors relating to the carbon atom:

$$\Delta_C(Q) = A[a_{CO}(Q) - 1] + B[a_{CD}(Q) - 1] + C[a_{CN}(Q) - 1] + D[a_{CC}(Q) - 1],$$

where

$$A = 2x(b_{^{nat}C} - b_{^{13}C})b_O, \quad B = 4x(1+x)(b_{^{nat}C} - b_{^{13}C})b_D,$$
$$C = 4x^2(b_{^{nat}C} - b_{^{13}C})b_N, \quad \text{and} \quad D = x^2(b_{^{nat}C}{}^2 - b_{^{13}C}{}^2). \quad (2)$$

The weighting factors *A*–*D* in Eq. 2 are numerically listed in Table 2.

The intramolecular contribution, $I_C^{intra}(Q)$, from the C···α pairs within the urea molecule is estimated by

$$I_C^{intra}(Q) = \Sigma 2x(b_{^{nat}C} - b_{^{13}C})b_\alpha \times \exp(-l_{C\alpha}{}^2Q^2/2)\sin(Qr_{C\alpha})/(Qr_{C\alpha}). \quad (3)$$

where, $l_{C\alpha}$ and $r_{C\alpha}$ denote the root-mean-square displacement and internuclear distance for the C···α pair, respectively. Values of $r_{C\alpha}$ and $l_{C\alpha}$ used for the present analysis were taken from the literature determined by the single crystal neutron diffraction work[23] and from values calculated for related molecules,[24,25] respectively. The calculated $I_C^{intra}(Q)$ was then subtracted from the observed $\Delta_C(Q)$ to obtain the intermolecular difference function, $\Delta_C^{inter}(Q)$,

$$\Delta_C^{inter}(Q) = \Delta_C(Q) - I_C^{intra}(Q). \quad (4)$$

The distribution function, $G_C(r)$, describing the structure around the carbonyl-carbon atom is obtained by the Fourier transform of the observed $\Delta_C(Q)$,

$$G_C(r) = 1 + (A+B+C+D)^{-1}(2\pi^2\rho r)^{-1} \times \int_0^{Q_{max}} Q\Delta_C(Q)\sin(Qr)dQ = [Ag_{CO}(r) + Bg_{CD}(r) + Cg_{CN}(r) + Dg_{CC}(r)] \times (A+B+C+D)^{-1}. \quad (5)$$

The upper limit of the integral, Q_{max}, was set to be 10.14 Å^{-1}. The intermolecular distribution function, $G_C^{inter}(r)$, was evaluated by the Fourier transform of the $\Delta_C^{inter}(Q)$.

Hydration parameters for the carbonyl group of the urea molecule were determined through the least-squares fitting procedure for the observed intermolecular $\Delta_C^{inter}(Q)$, employing the model function $\Delta_C^{model}(Q)$ involving both the short- and long-range contributions:[26–28]

$$\Delta_C^{model}(Q) = \Sigma 2xn_{C\alpha}(b_{^{nat}C} - b_{^{13}C})b_\alpha \times \exp(-l_{C\alpha}{}^2Q^2/2)\sin(Qr_{C\alpha})/(Qr_{C\alpha}) + 4\pi\rho(A+B+C+D)\exp(-l_0{}^2Q^2/2) \times [Qr_0\cos(Qr_0) - \sin(Qr_0)]Q^{-3}, \quad (6)$$

where, $n_{C\alpha}$ denotes the coordination number of α atom around the carbonyl-carbon atom. The long-range parameter, r_0, corresponds to the distance beyond which a continuous distribution of atoms around the C atom can be assumed. The parameter, l_0, describes the sharpness of the boundary at r_0. Structural parameters $n_{C\alpha}$, $l_{C\alpha}$, $r_{C\alpha}$, r_0, and l_0 are, respectively, determined from the least-squares fit to the observed $\Delta_C^{inter}(Q)$. The fitting procedure was performed in the range of $0.3 \leq Q \leq 10.1$ Å^{-1} with the SALS program,[29] assuming that the statistical uncertainties are distributed uniformly.

Table 2. Values of the Coefficients of $a_{ij}(Q)$ in Eq. 2

A/barns	B/barns	C/barns	D/barns
0.0079	0.0209	0.0038	0.0013

Results and Discussion

Observed scattering cross sections, $(d\sigma/d\Omega)^{obs}$, for aqueous 15 mol % urea solutions with different $^{12}C/^{13}C$ isotopic ratio of the carbonyl-carbon atom, ^{nat}C and ^{13}C, are shown in Figs. 1a and 1b, respectively. The decrease in $(d\sigma/d\Omega)^{obs}$ in

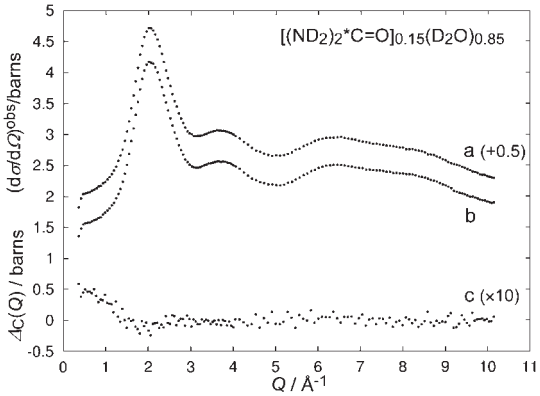

Fig. 1. Observed scattering cross sections $(d\sigma/d\Omega)^{obs}$ for aqueous 15 mol % urea solutions with different isotopic ratios of $^{12}C/^{13}C$. a) ^{nat}C (sample I). b) ^{13}C (sample II). c) Observed difference function $\Delta_C(Q)$.

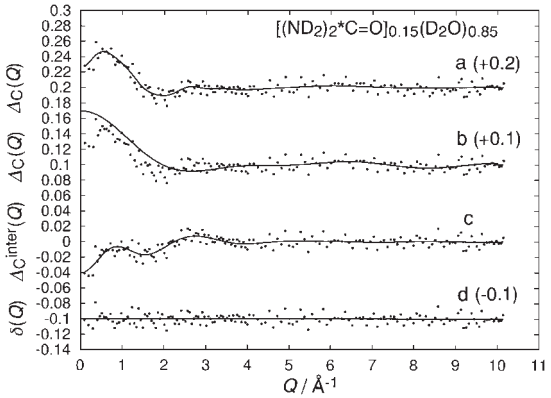

Fig. 2. a) $\Delta_C(Q)$ observed for aqueous 15 mol % urea solutions in D_2O (dots). Back Fourier transform of $G_C(r)$ in Fig. 3a (solid line). b) Observed $\Delta_C(Q)$ (dots) and intramolecular contribution (solid line). c) Intermolecular difference function, $\Delta_C^{inter}(Q)$ (dots), and the best-fit of the calculated $\Delta_C^{calc}(Q)$ (solid line). d) Residual functions (dots).

the higher-Q region is obviously due to an inelasticity effect. The overall features of $(d\sigma/d\Omega)^{obs}$ for the two solutions look very similar because of the small difference in the coherent scattering length between ^{12}C and ^{13}C nuclei. However, the first-order difference function $\Delta_C(Q)$ (Fig. 1c) derived from present scattering cross sections indicates an oscillational feature which is expected to include information about the environmental structure around the carbonyl-carbon atom. The observed difference function, $\Delta_C(Q)$, is represented in Fig. 2a. Although the data points are somewhat scattered because of relatively small difference in observed scattering cross sections between the ^{nat}C and ^{13}C samples, the diffraction peaks at $Q = 0.6$ and $2.6\,\text{Å}^{-1}$ and oscillational feature extending beyond the higher-Q region can be observed. The calculated intramolecular interference term (Fig. 2b) was then subtracted from the observed $\Delta_C(Q)$ to obtain the intermolecular difference function, $\Delta_C^{inter}(Q)$, as shown in Fig. 2c. The normalization factor, γ, defined by $I_C^{intra}(Q) = \gamma \times \Delta_C(Q)$ (in the sufficiently high-Q region), was obtained to be 0.93 ± 0.02 from the least-squares fit in the range of $4 \leq Q \leq 10\,\text{Å}^{-1}$. The result indicates that the

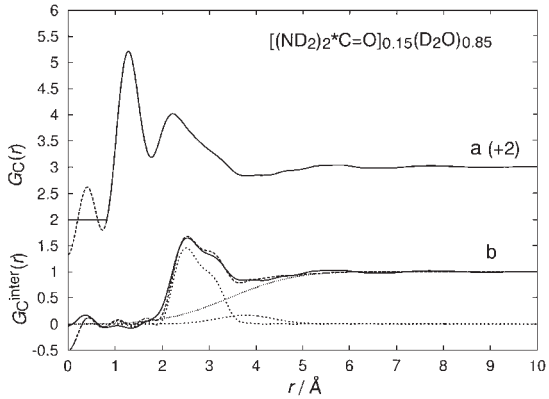

Fig. 3. a) Total distribution function around the carbonyl-carbon atom of the urea molecule, $G_C(r)$, observed for aqueous 15 mol % urea solutions in D_2O (solid line). b) Observed intermolecular distribution function, $G_C^{inter}(r)$ (solid line). Fourier transform of the calculated $\Delta_C^{calc}(Q)$ is shown by a broken line. The contributions from the short- and long-range interactions are denoted by the thick and thin dotted lines, respectively.

overall normalization error in the present $\Delta_C(Q)$ is ca. 7%. The present $\Delta_C^{inter}(Q)$ is characterized by resolved first and second diffraction peaks at $Q = 0.8$ and $2.7\,\text{Å}^{-1}$, respectively.

The total and intermolecular distribution function, $G_C(r)$ and $G_C^{inter}(r)$, are shown in Figs. 3a and 3b, respectively. A dominant first peak at $r \approx 1.3$ Å in the $G_C(r)$ is attributable to the sum of contributions from intramolecular C=O and C–N interactions within the urea molecule. The intramolecular non-bonding C–D_N (D_N: amino deuterium atom of the urea molecule) interaction can be seen as a partially resolved peak at $r \approx 2.2$ Å in the $G_C(r)$. The intermolecular first peak at $r \approx 2.5$ Å in the $G_C^{inter}(r)$ and a shoulder appearing at the higher-r side, may be assigned to the intermolecular interactions between the carbonyl-carbon atom and water molecules within the first hydration shell of the carbonyl group. Preliminary analysis of the present $G_C^{inter}(r)$ shows that the integrated value of the $G_C^{inter}(r)$ to the upper limit of $r = 3.6$ Å roughly corresponds to ca. $4D_2O$ molecules, however, the r-space resolution of the present $G_C^{inter}(r)$ is considered to be insufficient because of relatively small value of the upper limit of the Fourier integral ($Q_{max} = 10.14\,\text{Å}^{-1}$). Moreover, the present $G_C^{inter}(r)$ is regarded as an average quantity of the weighted partial distribution functions such as $g_{CO_C}(r)$, $g_{CO_W}(r)$, $g_{CD_N}(r)$, $g_{CD_W}(r)$, $g_{CN}(r)$, and $g_{CC}(r)$, where O_C denotes the carbonyl-oxygen atom within the urea molecule. In order to evaluate the $O_C \cdots D_W$ and $O_C \cdots O_W$ coordination numbers, information on the above partial distribution functions is necessary, i.e., it is difficult to determine the number of D_2O molecules in the first coordination shell of the carbonyl group from an integration value derived from the present $G_C^{inter}(r)$. In the present analysis, parameters concerning the hydration structure around the carbonyl-carbon atom were determined through the least-squares fit of the observed $\Delta_C^{inter}(Q)$. This procedure can avoid uncertainties associated with truncation errors arising from the Fourier transformation. The least-squares fitting procedure employing a model function involving the short- and long-range interactions was used in the analysis of the first-order differ-

ence functions, $\Delta_N(Q)$ and $\Delta_C(Q)$ that were observed for concentrated aqueous urea and sodium acetate solutions, respectively.[13,15] In the present fitting procedure, the following assumptions were adopted in evaluating the parameters in Eq. 6. a) Parameters for the first nearest neighbor C···D_2O interaction, $r_{CD_{W1}}$, $l_{CD_{W1}}$, l_{CO_W}, $l_{CD_{W2}}$, and $n_{CD_{W1}}$, were refined independently. The bond angle α (=$\angle$C···D_{W1}–O_W) and the dihedral angle β between the plane involving atoms C, D_{W1}, and O_W, and the molecule plane of the D_2O molecule, were treated as independent parameters. The geometry of the D_2O molecule was fixed to that reported for liquid heavy water ($r_{OD} = 0.983$ Å, $r_{DD} = 1.55$ Å).[30,31] b) The second nearest neighbor C···D_2O interaction was also taken into account in the present model function, in which the contribution was treated as a single interaction with the coherent scattering length in Eq. 6, b_α, being $2b_D + b_O$. c) Structural parameters for long-range random distribution of atoms, l_0 and r_0, were allowed to vary independently.

The results of the least-squares fit for the observed $\Delta_C^{inter}(Q)$ are shown in Fig. 2c. Satisfactory agreement was obtained between observed and calculated structure functions. The Fourier transform of the calculated $\Delta_C^{model}(Q)$ ($Q_{max} = 10.14$ Å^{-1}) was also in good agreement with the observed $G_C^{inter}(r)$ as depicted in Fig. 3b. Final values of all of the independent parameters are summarized in Table 3. The present value of the hydration number of the carbonyl group, $n_{CD_{W1}} = 4.3(3)$ is much larger than that reported for a more concentrated aqueous 20 mol % urea solution by means of the neutron diffraction combined with the EPSR simulation ($n_{O_C\cdots H_w} = 1.70$)[14] and that derived from MD simulation for a more dilute solution (one urea and 1616 SPC/E water molecules), $n_{O_C\cdots H_w} = 1.8$–1.9.[4] The present hydration number of the carbonyl group suggests strong hydrogen-bonded interactions between the carbonyl-oxygen atom and the neighboring water molecules. The average $\angle$C···D_{W1}–O_W angle was determined to be 124(5)° with an intermolecular C···D_{W1} distance of 2.46(3) Å. These values are consistent with the hydration geometry that one of the deuterium atoms in D_2O forms a hydrogen bond to the carboxyl-oxygen atom with the interatomic distance of $r_{O_CD_w} = 1.8$–1.9 Å. The second nearest neighbor C···D_2O interaction may involve the water molecules hydrogen bonded to the amino-deuterium atoms of the urea molecule, which have been reported previously.[13] Åstrand et al. have shown that the intermolecular distribution function $G_C(r)$ predicted for the aqueous 2 m (3.5 mol %) urea solution by MD method.[2] They found the first intermolecular peak at $r = 2.85$ Å. If this first peak is attributable to the nearest neighbor C···D_W interaction, the predicted peak position by MD simulation is ca. 0.4 Å larger than that observed in the present study. The C···O_W partial distribution function has been calculated for more concentrated aqueous 8.2 m (12.9 mol %) urea solution by Weerasinghe and Smith.[6] The position of the first peak in the predicted $g_{CO_W}(r)$ (ca. 3.8 Å) is obviously larger than the nearest neighbor C···O_W distance (3.12 Å) which was determined from the present values of $r_{CD_{W1}}$, α, and β. According to the MD study by Åstrand et al.[2] and the neutron diffraction with the EPSR analysis by Soper et al.,[14] there is a considerable amount of urea dimer or clusters present in aqueous solutions. In such a case, the first and second peaks observed in the present $G_C^{inter}(r)$ might involve contributions from the nearest neighbor urea–urea interaction. On the other hand, Raman spectroscopic results do not indicate the presence of the urea dimer in aqueous solutions of the urea concentration below 9.1 mol % (molar ratio of the urea and water molecules is 1:10).[32] In order to examine the presence of the urea dimer or clusters in the aqueous solutions, it is necessary to obtain a N–N partial distribution function, which requires additional neutron diffraction measurements on at least three samples with different $^{14}N/^{15}N$ isotopic compositions. This will be a future research subject.

Table 3. Results of the Least-Squares Refinement for the $\Delta_C^{inter}(Q)$ Observed for Aqueous 15 mol % Urea Solutions in D_2O[a)]

Interaction	i···j	r_{ij}/Å	l_{ij}/Å	n_{ij}
C···D_2O(I)	C···D_{W1}	2.46(3)	0.20(8)	4.3(3)
	C···O_W	(3.12)[b)]	0.25(5)	(4.3)[c)]
	C···D_{W2}	(2.85)[b)]	0.29(5)	(4.3)[c)]
		$\alpha = 124(5)°$ [d)]	$\beta = -2(10)°$ [e)]	
C···D_2O(II)	C···D_2O	3.9(2)	0.6(2)	1.5(5)
		r_0/Å	l_0/Å	
C···X[f)]		3.75(3)	1.06(2)	

a) Estimated errors are given in parentheses. b) Calculated from values $r_{CD_{W1}} = 2.46$ Å, $\alpha = 124°$, and $\beta = -2°$. c) Fixed at the value $n_{CD_{W1}}$. d) Bond angle $\angle$C···D–O_W. e) Dihedral angle between the plane involving the C···D–O_W atoms and molecular plane of D_2O. f) X: O, D, N, and C.

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