Table SI. Cross-correlated relaxation (CCR) rates between dipolar couplings of two CH bonds (σ_{obs}) in the methyl groups of ubiquitin measured at fourteen temperatures [a]

	σ_{obs}^{275K} (s^{-1})	σ_{obs}^{278K} (s^{-1})	σ_{obs}^{281K} (s^{-1})	σ_{obs}^{283K} (s^{-1})	σ_{obs}^{286K} (s^{-1})	σ_{obs}^{288K} (s^{-1})	σ_{obs}^{291K} (s^{-1})
I3γ2	10.67 ± 0.21	9.36 ± 0.16	8.41 ± 0.14	7.69 ± 0.12	6.80 ± 0.09	6.28 ± 0.10	5.69 ± 0.09
I3δ1	8.97 ± 0.20	7.83 ± 0.15	6.99 ± 0.14	6.35 ± 0.12	5.68 ± 0.09	5.23 ± 0.10	4.77 ± 0.10
T7γ2	9.66 ± 0.27	8.36 ± 0.20	7.58 ± 0.18	6.90 ± 0.15	6.09 ± 0.11	5.64 ± 0.12	5.11 ± 0.12
L8δ1	4.47 ± 0.09	3.80 ± 0.08	3.46 ± 0.07	3.16 ± 0.06	2.68 ± 0.05	2.53 ± 0.05	2.20 ± 0.05
T9γ2	7.58 ± 0.16	6.61 ± 0.13	5.96 ± 0.12	5.46 ± 0.10	4.74 ± 0.08	4.38 ± 0.09	3.95 ± 0.09
T12γ2	9.06 ± 0.23	7.78 ± 0.18	6.97 ± 0.16	6.35 ± 0.13	5.45 ± 0.10	5.13 ± 0.11	4.53 ± 0.11
I13δ1	6.76 ± 0.17	5.97 ± 0.13	5.27 ± 0.12	4.86 ± 0.10	4.34 ± 0.08	3.94 ± 0.09	3.54 ± 0.09
V17γ2	9.27 ± 0.23	8.03 ± 0.17	7.24 ± 0.15	6.59 ± 0.12	5.77 ± 0.09	5.38 ± 0.10	4.90 ± 0.10
T22γ2	10.59 ± 0.26	9.18 ± 0.20	8.42 ± 0.18	7.67 ± 0.14	6.76 ± 0.11	6.37 ± 0.12	5.68 ± 0.12
I23γ2	10.45 ± 0.25	9.27 ± 0.18	8.29 ± 0.16	7.59 ± 0.13	6.72 ± 0.09	6.28 ± 0.10	5.63 ± 0.10
I23δ1	6.67 ± 0.20	5.65 ± 0.15	5.06 ± 0.14	4.56 ± 0.12	4.02 ± 0.09	3.66 ± 0.10	3.29 ± 0.10
I36γ2	8.03 ± 0.21	7.11 ± 0.16	6.44 ± 0.14	6.06 ± 0.12	5.45 ± 0.09	5.17 ± 0.09	4.66 ± 0.09
I36δ1	6.91 ± 0.16	5.97 ± 0.13	5.43 ± 0.12	4.94 ± 0.10	4.33 ± 0.08	4.10 ± 0.09	3.63 ± 0.09
L43δ2	6.63 ± 0.22	5.77 ± 0.16	5.09 ± 0.15	4.48 ± 0.12	4.04 ± 0.09	3.53 ± 0.11	3.31 ± 0.09
I44δ1	3.18 ± 0.14	2.71 ± 0.12	2.48 ± 0.11	2.20 ± 0.09	1.91 ± 0.07	1.79 ± 0.08	1.57 ± 0.08
L50δ2	9.47 ± 0.35	8.43 ± 0.25	7.51 ± 0.22	6.89 ± 0.18	6.04 ± 0.13	5.61 ± 0.15	5.03 ± 0.14
L56δ2	8.70 ± 0.29	7.72 ± 0.20	6.89 ± 0.18	6.28 ± 0.15	5.63 ± 0.11	4.99 ± 0.12	4.58 ± 0.12
I61γ2	9.93 ± 0.21	8.72 ± 0.15	7.85 ± 0.14	7.18 ± 0.11	6.36 ± 0.08	5.91 ± 0.09	5.34 ± 0.09
I61δ1	7.47 ± 0.22	6.45 ± 0.17	5.75 ± 0.16	5.19 ± 0.13	4.55 ± 0.10	4.18 ± 0.11	3.72 ± 0.11
L67δ2	3.83 ± 0.11	3.39 ± 0.09	2.99 ± 0.08	2.68 ± 0.07	2.38 ± 0.05	2.14 ± 0.06	1.95 ± 0.06
V70γ2	5.09 ± 0.14	4.44 ± 0.11	3.95 ± 0.10	3.55 ± 0.08	3.06 ± 0.06	2.74 ± 0.07	2.46 ± 0.07
L73δ1	2.69 ± 0.05	2.35 ± 0.04	2.15 ± 0.04	1.94 ± 0.03	1.73 ± 0.03	1.61 ± 0.03	1.47 ± 0.03

[a] σ_{obs} was calculated using $\sigma_{obs} = \frac{1}{8\Delta}\ln\frac{9I_{\alpha^2\beta}I_{\alpha\beta^2}}{I_{\alpha^3}I_{\beta^3}}$. All errors ($\Delta\sigma_{obs}$) were determined from $\Delta\sigma_{obs} = \frac{q}{8\Delta}\left(\frac{1}{I_{\alpha^3}}+\frac{1}{I_{\alpha^2\beta}}+\frac{1}{I_{\alpha\beta^2}}+\frac{1}{I_{\beta^3}}\right)$, where q is the noise estimation from NMRPipe, Δ is the constant time evolution and I_i is the intensity of each peak in the quartet ($i = \alpha^3, \alpha^2\beta, \alpha\beta^2, \beta^3$).

Table SI. Cross-correlated relaxation (CCR) rates between dipolar couplings of two CH bonds (σ_{obs}) in the methyl groups of ubiquitin measured at fourteen temperatures [a] *(Continued)*

	σ_{obs}^{293K} (s^{-1})	σ_{obs}^{296K} (s^{-1})	σ_{obs}^{298K} (s^{-1})	σ_{obs}^{301K} (s^{-1})	σ_{obs}^{303K} (s^{-1})	σ_{obs}^{305K} (s^{-1})	σ_{obs}^{308K} (s^{-1})
I3γ2	5.34 ± 0.07	4.84 ± 0.06	4.52 ± 0.07	4.15 ± 0.05	3.94 ± 0.06	3.69 ± 0.05	3.42 ± 0.05
I3δ1	4.46 ± 0.08	4.02 ± 0.07	3.77 ± 0.07	3.52 ± 0.05	3.24 ± 0.06	3.09 ± 0.05	2.83 ± 0.05
T7γ2	4.80 ± 0.09	4.43 ± 0.08	4.16 ± 0.08	3.90 ± 0.06	3.74 ± 0.07	3.52 ± 0.06	3.23 ± 0.06
L8δ1	2.04 ± 0.04	1.84 ± 0.04	1.70 ± 0.04	1.55 ± 0.03	1.49 ± 0.04	1.44 ± 0.03	1.32 ± 0.03
T9γ2	3.67 ± 0.07	3.32 ± 0.06	3.11 ± 0.07	2.79 ± 0.05	2.72 ± 0.06	2.54 ± 0.05	2.36 ± 0.05
T12γ2	4.20 ± 0.09	3.85 ± 0.07	3.60 ± 0.08	3.20 ± 0.06	3.09 ± 0.07	2.89 ± 0.06	2.63 ± 0.06
I13δ1	3.29 ± 0.07	2.97 ± 0.06	2.76 ± 0.07	2.54 ± 0.05	2.35 ± 0.06	2.17 ± 0.05	2.04 ± 0.05
V17γ2	4.55 ± 0.07	4.09 ± 0.06	3.79 ± 0.06	3.46 ± 0.04	3.26 ± 0.06	3.13 ± 0.04	2.90 ± 0.04
T22γ2	5.26 ± 0.09	4.74 ± 0.08	4.48 ± 0.08	4.06 ± 0.06	3.82 ± 0.07	3.74 ± 0.06	3.35 ± 0.06
I23γ2	5.27 ± 0.08	4.79 ± 0.06	4.42 ± 0.07	4.13 ± 0.05	3.89 ± 0.06	3.71 ± 0.05	3.45 ± 0.05
I23δ1	3.03 ± 0.08	2.73 ± 0.06	2.54 ± 0.07	2.28 ± 0.05	2.11 ± 0.06	1.97 ± 0.05	1.79 ± 0.05
I36γ2	4.42 ± 0.07	4.02 ± 0.06	3.94 ± 0.06	3.54 ± 0.04	3.36 ± 0.05	3.19 ± 0.04	2.91 ± 0.04
I36δ1	3.41 ± 0.07	3.04 ± 0.06	2.82 ± 0.06	2.58 ± 0.05	2.44 ± 0.06	2.29 ± 0.05	2.12 ± 0.05
L43δ2	3.06 ± 0.07	2.76 ± 0.06	2.60 ± 0.07	2.37 ± 0.05	2.19 ± 0.06	2.01 ± 0.05	1.83 ± 0.05
I44δ1	1.45 ± 0.07	1.24 ± 0.06	1.19 ± 0.06	1.03 ± 0.04	1.01 ± 0.06	0.92 ± 0.05	0.77 ± 0.05
L50δ2	4.64 ± 0.11	4.16 ± 0.09	3.85 ± 0.10	3.43 ± 0.07	3.16 ± 0.09	3.02 ± 0.07	2.84 ± 0.07
L56δ2	4.19 ± 0.09	3.82 ± 0.08	3.50 ± 0.08	3.17 ± 0.06	2.89 ± 0.07	2.73 ± 0.06	2.54 ± 0.06
I61γ2	5.01 ± 0.07	4.57 ± 0.06	4.24 ± 0.06	3.91 ± 0.04	3.69 ± 0.06	3.49 ± 0.04	3.22 ± 0.05
I61δ1	3.44 ± 0.09	3.03 ± 0.07	2.82 ± 0.08	2.56 ± 0.05	2.27 ± 0.07	2.13 ± 0.06	1.96 ± 0.06
L67δ2	1.81 ± 0.05	1.64 ± 0.04	1.53 ± 0.04	1.37 ± 0.03	1.30 ± 0.04	1.18 ± 0.03	1.12 ± 0.03
V70γ2	2.27 ± 0.05	2.07 ± 0.05	1.95 ± 0.05	1.80 ± 0.04	1.70 ± 0.04	1.64 ± 0.04	1.53 ± 0.04
L73δ1	1.36 ± 0.03	1.25 ± 0.02	1.21 ± 0.03	1.10 ± 0.02	1.04 ± 0.02	1.00 ± 0.02	0.94 ± 0.02

[a] σ_{obs} was calculated using $\sigma_{obs} = \frac{1}{8\Delta}\ln\frac{9I_{\alpha^2\beta}I_{\alpha\beta^2}}{I_{\alpha^3}I_{\beta^3}}$. All errors ($\Delta\sigma_{obs}$) were determined from $\Delta\sigma_{obs} = \frac{q}{8\Delta}\left(\frac{1}{I_{\alpha^3}}+\frac{1}{I_{\alpha^2\beta}}+\frac{1}{I_{\alpha\beta^2}}+\frac{1}{I_{\beta^3}}\right)$, where q is the noise estimation from NMRPipe, Δ is the constant time evolution and I_i is the intensity of each peak in the quartet ($i = \alpha^3, \alpha^2\beta, \alpha\beta^2, \beta^3$).

Table SII. Methyl group order parameters (S^2_{axis}) calculated at fourteen temperatures [a]

	275 K	278 K	281 K	283 K	286 K	288 K	291 K
	τ_c (ns) 11.45	τ_c (ns) 10.23	τ_c (ns) 9.17	τ_c (ns) 8.55	τ_c (ns) 7.72	τ_c (ns) 7.22	τ_c (ns) 6.55
	σ_{rigid} (s^{-1}) 10.95	σ_{rigid} (s^{-1}) 9.80	σ_{rigid} (s^{-1}) 8.79	σ_{rigid} (s^{-1}) 8.21	σ_{rigid} (s^{-1}) 7.42	σ_{rigid} (s^{-1}) 6.95	σ_{rigid} (s^{-1}) 6.32
	S^2_{axis}	S^2_{axis}	S^2_{axis}	S^2_{axis}	S^2_{axis}	S^2_{axis}	S^2_{axis}
I3γ2	0.97 ± 0.02	0.96 ± 0.02	0.96 ± 0.02	0.94 ± 0.01	0.92 ± 0.01	0.90 ± 0.01	0.90 ± 0.01
I3δ1	0.82 ± 0.02	0.80 ± 0.02	0.80 ± 0.02	0.77 ± 0.01	0.77 ± 0.01	0.75 ± 0.01	0.75 ± 0.02
T7γ2	0.88 ± 0.02	0.85 ± 0.02	0.86 ± 0.02	0.84 ± 0.02	0.82 ± 0.01	0.81 ± 0.02	0.81 ± 0.02
L8δ1	0.41 ± 0.01	0.39 ± 0.01	0.39 ± 0.01	0.38 ± 0.01	0.36 ± 0.01	0.36 ± 0.01	0.35 ± 0.01
T9γ2	0.69 ± 0.01	0.68 ± 0.01	0.68 ± 0.01	0.67 ± 0.01	0.64 ± 0.01	0.63 ± 0.01	0.63 ± 0.01
T12γ2	0.83 ± 0.02	0.79 ± 0.02	0.79 ± 0.02	0.77 ± 0.02	0.73 ± 0.01	0.74 ± 0.02	0.72 ± 0.02
I13δ1	0.62 ± 0.02	0.61 ± 0.01	0.60 ± 0.01	0.59 ± 0.01	0.58 ± 0.01	0.57 ± 0.01	0.56 ± 0.01
V17γ2	0.84 ± 0.02	0.82 ± 0.02	0.82 ± 0.02	0.80 ± 0.01	0.78 ± 0.01	0.77 ± 0.01	0.78 ± 0.02
T22γ2	0.97 ± 0.02	0.94 ± 0.02	0.96 ± 0.02	0.93 ± 0.02	0.91 ± 0.01	0.92 ± 0.02	0.90 ± 0.02
I23γ2	0.95 ± 0.02	0.94 ± 0.02	0.94 ± 0.02	0.92 ± 0.02	0.90 ± 0.01	0.90 ± 0.01	0.89 ± 0.02
I23δ1	0.61 ± 0.02	0.58 ± 0.02	0.58 ± 0.02	0.56 ± 0.01	0.54 ± 0.01	0.53 ± 0.01	0.52 ± 0.02
I36γ2	0.73 ± 0.02	0.73 ± 0.02	0.73 ± 0.02	0.74 ± 0.01	0.73 ± 0.01	0.74 ± 0.01	0.74 ± 0.01
I36δ1	0.63 ± 0.02	0.61 ± 0.01	0.62 ± 0.01	0.60 ± 0.01	0.58 ± 0.01	0.59 ± 0.01	0.57 ± 0.01
L43δ2	0.60 ± 0.02	0.59 ± 0.02	0.58 ± 0.02	0.55 ± 0.01	0.54 ± 0.01	0.51 ± 0.02	0.52 ± 0.02
I44δ1	0.29 ± 0.01	0.28 ± 0.01	0.28 ± 0.01	0.27 ± 0.01	0.26 ± 0.01	0.26 ± 0.01	0.25 ± 0.01
L50δ2	0.87 ± 0.03	0.86 ± 0.03	0.85 ± 0.03	0.84 ± 0.02	0.81 ± 0.02	0.81 ± 0.02	0.80 ± 0.02
L56δ2	0.79 ± 0.03	0.79 ± 0.02	0.78 ± 0.02	0.77 ± 0.02	0.76 ± 0.01	0.72 ± 0.02	0.73 ± 0.02
I61γ2	0.91 ± 0.02	0.89 ± 0.02	0.89 ± 0.02	0.87 ± 0.01	0.86 ± 0.01	0.85 ± 0.01	0.85 ± 0.01
I61δ1	0.68 ± 0.02	0.66 ± 0.02	0.65 ± 0.02	0.63 ± 0.02	0.61 ± 0.01	0.60 ± 0.02	0.59 ± 0.02
L67δ2	0.35 ± 0.01	0.35 ± 0.01	0.34 ± 0.01	0.33 ± 0.01	0.32 ± 0.01	0.31 ± 0.01	0.31 ± 0.01
V70γ2	0.46 ± 0.01	0.45 ± 0.01	0.45 ± 0.01	0.43 ± 0.01	0.41 ± 0.01	0.39 ± 0.01	0.39 ± 0.01
L73δ1	0.25 ± 0.01	0.24 ± 0.00	0.24 ± 0.00	0.24 ± 0.00	0.23 ± 0.00	0.23 ± 0.00	0.23 ± 0.01

[a] Given at each temperature are the rotational correlation time (τ_c) and the CCR rate between dipolar couplings of two CH bonds in the absence of local motion (σ_{rigid}). σ_{rigid} is calculated using $\sigma_{rigid} = \frac{1}{45}\tau_c\left(\frac{\mu_0 h\gamma_H\gamma_C}{8\pi^2 r^3_{CH}}\right)^2\left(2+\frac{3}{2(1+(\omega_c\tau_c)^2)}\right)$, where μ_o is the permeability of a vacuum, h is the Planck constant, γ_H and γ_C are the gyromagnetic ratios of ^{1}H and ^{13}C, respectively, r_{CH} is the CH bond length, ω_C is the Larmor frequency of ^{13}C and τ_c is the rotational correlation time. S^2_{axis} is derived from $S^2_{axis} = \frac{\sigma_{obs}}{\sigma_{rigid}}$. The error (ΔS^2_{axis}) is determined using $\Delta S^2_{axis} = \frac{\Delta\sigma_{obs}}{\sigma_{rigid}}$.

Table SII. Methyl groups order parameters (S^2_{axis}) calculated at fourteen different temperatures [a] *(continued)*

	293 K	296 K	298 K	301 K	303 K	305 K	308 K
τ_c (ns)	6.15	5.61	5.28	4.84	4.57	4.32	3.98
σ_{rigid} (s^{-1})	5.95	5.44	5.13	4.72	4.47	4.24	3.93
	S^2_{axis}	S^2_{axis}	S^2_{axis}	S^2_{axis}	S^2_{axis}	S^2_{axis}	S^2_{axis}
I3γ2	0.90 ± 0.01	0.89 ± 0.01	0.88 ± 0.01	0.88 ± 0.01	0.88 ± 0.01	0.87 ± 0.01	0.87 ± 0.01
I3δ1	0.75 ± 0.01	0.74 ± 0.01	0.73 ± 0.01	0.74 ± 0.01	0.72 ± 0.01	0.73 ± 0.01	0.72 ± 0.01
T7γ2	0.81 ± 0.02	0.81 ± 0.01	0.81 ± 0.02	0.82 ± 0.01	0.84 ± 0.02	0.83 ± 0.01	0.82 ± 0.01
L8δ1	0.34 ± 0.01	0.34 ± 0.01	0.33 ± 0.01	0.33 ± 0.01	0.33 ± 0.01	0.34 ± 0.01	0.34 ± 0.01
T9γ2	0.62 ± 0.01	0.61 ± 0.01	0.61 ± 0.01	0.59 ± 0.01	0.61 ± 0.01	0.60 ± 0.01	0.60 ± 0.01
T12γ2	0.71 ± 0.01	0.71 ± 0.01	0.70 ± 0.02	0.68 ± 0.01	0.69 ± 0.02	0.68 ± 0.01	0.67 ± 0.02
I13δ1	0.55 ± 0.01	0.55 ± 0.01	0.54 ± 0.01	0.54 ± 0.01	0.53 ± 0.01	0.51 ± 0.01	0.52 ± 0.01
V17γ2	0.76 ± 0.01	0.75 ± 0.01	0.74 ± 0.01	0.73 ± 0.01	0.73 ± 0.01	0.74 ± 0.01	0.74 ± 0.01
T22γ2	0.88 ± 0.02	0.87 ± 0.01	0.87 ± 0.02	0.86 ± 0.01	0.85 ± 0.02	0.88 ± 0.01	0.85 ± 0.02
I23γ2	0.88 ± 0.01	0.88 ± 0.01	0.86 ± 0.01	0.88 ± 0.01	0.87 ± 0.01	0.88 ± 0.01	0.88 ± 0.01
I23δ1	0.51 ± 0.01	0.50 ± 0.01	0.49 ± 0.01	0.48 ± 0.01	0.47 ± 0.01	0.46 ± 0.01	0.46 ± 0.01
I36γ2	0.74 ± 0.01	0.74 ± 0.01	0.77 ± 0.01	0.75 ± 0.01	0.75 ± 0.01	0.75 ± 0.01	0.74 ± 0.01
I36δ1	0.57 ± 0.01	0.56 ± 0.01	0.55 ± 0.01	0.55 ± 0.01	0.55 ± 0.01	0.54 ± 0.01	0.54 ± 0.01
L43δ2	0.52 ± 0.01	0.51 ± 0.01	0.51 ± 0.01	0.50 ± 0.01	0.49 ± 0.01	0.47 ± 0.01	0.47 ± 0.01
I44δ1	0.24 ± 0.01	0.23 ± 0.01	0.23 ± 0.01	0.22 ± 0.01	0.23 ± 0.01	0.22 ± 0.01	0.20 ± 0.01
L50δ2	0.78 ± 0.02	0.76 ± 0.02	0.75 ± 0.02	0.73 ± 0.01	0.71 ± 0.02	0.71 ± 0.02	0.72 ± 0.02
L56δ2	0.70 ± 0.02	0.70 ± 0.01	0.68 ± 0.02	0.67 ± 0.01	0.65 ± 0.02	0.64 ± 0.01	0.65 ± 0.02
I61γ2	0.84 ± 0.01	0.84 ± 0.01	0.83 ± 0.01	0.83 ± 0.01	0.82 ± 0.01	0.82 ± 0.01	0.82 ± 0.01
I61δ1	0.58 ± 0.01	0.56 ± 0.01	0.55 ± 0.02	0.54 ± 0.01	0.51 ± 0.02	0.50 ± 0.01	0.50 ± 0.01
L67δ2	0.30 ± 0.01	0.30 ± 0.01	0.30 ± 0.01	0.29 ± 0.01	0.29 ± 0.01	0.28 ± 0.01	0.29 ± 0.01
V70γ2	0.38 ± 0.01	0.38 ± 0.01	0.38 ± 0.01	0.38 ± 0.01	0.38 ± 0.01	0.39 ± 0.01	0.39 ± 0.01
L73δ1	0.23 ± 0.01	0.23 ± 0.00	0.24 ± 0.01	0.23 ± 0.00	0.23 ± 0.01	0.24 ± 0.00	0.24 ± 0.01

[a]Given at each temperature are the rotational correlation time (τ_c) and the CCR rate between dipolar couplings of two CH bonds in the absence of local motion (σ_{rigid}). σ_{rigid} is calculated using $\sigma_{rigid} = \frac{1}{45}\tau_c\left(\frac{\mu_0 h\gamma_H\gamma_C}{8\pi^2 r_{CH}^3}\right)^2\left(2+\frac{3}{2(1+(\omega_c\tau_c)^2)}\right)$, where μ_o is the permeability of a vacuum, h is the Planck constant, γ_H and γ_C are the gyromagnetic ratios of ^1H and ^{13}C, respectively, r_{CH} is the CH bond length, ω_C is the Larmor frequency of ^{13}C and τ_c is the rotational correlation time. S^2_{axis} is derived from $S^2_{axis} = \frac{\sigma_{obs}}{\sigma_{rigid}}$. The error (ΔS^2_{axis}) is determined using $\Delta S^2_{axis} = \frac{\Delta\sigma_{obs}}{\sigma_{rigid}}$.