Mode Specific Vibrational Energy Relaxation of Amide I' and II' Modes in N-Methylacetamide/Water Clusters: Intra- and Inter-Molecular Energy Transfer Mechanisms

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Optimized cartesian coordinates of NMA-d_1.

B3LYP/aug-cc-pvdz HF=-248.5608904

N	-0.625605	-0.632862 0.000000
H	-0.496980	-1.633350 0.000000
C	0.486829	0.164304 0.000000
C	1.818257	-0.566175 0.000000
H	1.719655	-1.659737 0.000000
H	2.387858	-0.256002 -0.885409
H	2.387858	-0.256001 0.885409
C	-1.978992	-0.102015 0.000000
H	-1.905715	0.989912 -0.000002
H	-2.530481	-0.425306 -0.894502
H	-2.530480	-0.425304 0.894503
O	0.423870	1.389892 0.000000

Optimized cartesian coordinates of NMA-$d_1/(D_2O)_1$.

B3LYP/aug-cc-pvdz HF=-325.0168999

N	0.764903	1.072043 0.000166
H	1.593914	1.645873 0.000308
C	0.911875	-0.276441 0.000090
C	2.332266	-0.804654 0.000227
H	3.091559	-0.012525 0.000373
H	2.471140	-1.438100 0.885662
H	2.471355	-1.437979 -0.885260
C	-0.543879	1.718178 0.000051
H	-1.123009	1.431280 0.886661
H	-0.394362	2.802882 0.000143
H	-1.122793	1.431401 -0.886739
O	-0.054995	-1.044310 -0.000081
O	-2.863266	-0.633845 -0.000388
H	-1.905657	-0.828233 -0.000286
H	-3.291953	-1.496158 -0.000491

Optimized cartesian coordinates of NMA-$d_1/(D_2O)_2$.

B3LYP/aug-cc-pvdz HF=-401.4715048

N	1.033212	-1.454231 -0.033516
H	1.054883	-2.459507 0.044038
C	-0.165673	-0.837259 0.042683
C	-1.380483	-1.716082 0.233737
H	-1.140330	-2.786074 0.217698
H	-1.851941	-1.463858 1.192492
H	-2.112504	-1.489485 -0.551091
C	2.289472	-0.732555 -0.217470
H	2.501602	-0.079503 0.638028
H	3.095425	-1.465610 -0.324594
H	2.245593	-0.107715 -1.117738
O	-0.267169	0.399129 -0.037836
O	1.715752	2.458425 0.179793
H	0.991393	1.810486 0.095265
H	1.282296	3.304864 0.331821
O	-3.014636	1.092412 -0.162726
H	-3.188824	2.019811 -0.355131
H	-2.041547	1.011848 -0.123721

Optimized cartesian coordinates of NMA-$d_1/(D_2O)_3$.

B3LYP/aug-cc-pvdz HF=-477.9247724

N	1.064836	0.506400 -0.000668
H	2.021880	0.170837 -0.000225
C	0.062921	-0.392133 0.000121
C	0.453034	-1.853034 0.001600
H	1.539174	-1.998064 0.001608
H	0.014028	-2.337165 0.883205
H	0.013749	-2.339047 -0.878825
C	0.828121	1.945459 -0.002181
H	0.259192	2.253438 0.884158
H	1.798994	2.451458 -0.003232
H	0.258373	2.251340 -0.888717
O	-1.134747	-0.046039 -0.000339
O	-2.408714	2.507522 0.001780
H	-2.010625	1.615477 0.000988
H	-3.359977	2.358044 0.003699
O	-2.812401	-2.319262 -0.001019
H	-3.748710	-2.094392 -0.003075
H	-2.339425	-1.462376 -0.000820
O	3.972342	-0.359821 0.000497
H	4.551710	-0.438436 -0.766805
H	4.551492	-0.436868 0.768123

Optimized cartesian coordinates of NMA-$d_1/(D_2O)_3$/PCM.

B3LYP/aug-cc-pvdz HF=-477.9566507

N	1.155910	0.504281 0.018518
H	2.129954	0.191140 0.011650
C	0.181763	-0.411034 -0.016974
C	0.601883	-1.860915 -0.062468
H	1.690512	-1.978847 -0.057309
H	0.172015	-2.383721 0.802379
H	0.187621	-2.323348 -0.968480
C	0.888138	1.935684 0.064805
H	0.288291	2.194633 0.947461
H	1.846852	2.461610 0.116048
H	0.344920	2.265274 -0.831115
O	-1.033426	-0.094110 -0.013009
O	-2.606018	2.258210 -0.044566
H	-2.025943	1.470388 -0.043163
H	-3.494326	1.913263 -0.239739
O	-3.045649	-2.047713 0.013030
H	-3.773249	-1.663005 0.531666
H	-2.340836	-1.365359 0.023862
O	3.923782	-0.370148 0.000576
H	4.471946	-0.108477 -0.763381
H	4.470663	-0.155837 0.780063

The identified important energy transfer pathway from the excited system mode from B3LYP/aug-cc-pvdz calculation.

(α, β): the bath mode combination
ω: bath mode frequencies (cm^{-1})
$C_{S\alpha\beta}$: third order coupling constant (kcal/mol/Å^3)
$\Delta\omega$: frequency difference $\tilde{\omega}_S - \omega_\alpha - \omega_\beta$ (cm^{-1})
$r_{S\alpha\beta}$: third order Fermi resonance parameter

Amide I' mode of NMA-d_1

(α,β)	ω	$\lvert C_{S\alpha\beta}\rvert$	$\lvert\Delta\omega\rvert$	$r_{S\alpha\beta}$
9 + 9	854.3 + 854.3	3.977	29.7	0.093
10 + 10	929.3 + 929.3	12.618	179.6	0.045
12 + 7	1035.6 + 608.5	5.572	34.9	0.119
15 + 6	1185.0 + 428.6	2.580	65.4	0.033
17 + 4	1411.5 + 283.4	2.095	15.9	0.123
19 + 2	1443.7 + 63.1	3.240	172.2	0.037

Amide I' mode of NMA-d_1/$(D_2O)_3$

(α,β)	ω	$\lvert C_{S\alpha\beta}\rvert$	$\lvert\Delta\omega\rvert$	$r_{S\alpha\beta}$
27 + 26	878.2 + 632.3	3.583	69.6	0.042
29 + 22	1015.9 + 443.6	4.235	120.5	0.032
30 + 24	1046.8 + 515.4	3.189	17.8	0.149
32 + 22	1140.8 + 443.6	0.769	4.4	0.150
35 + 19	1203.6 + 302.7	2.942	73.8	0.040
35 + 20	1203.6 + 312.7	2.156	63.8	0.034
36 + 19	1217.7 + 302.7	2.272	59.7	0.038
36 + 20	1217.7 + 312.7	3.700	49.7	0.073
40 + 7	1452.0 + 78.8	1.896	49.3	0.069
40 + 11	1452.0 + 108.2	2.731	19.8	0.212
40 + 13	1452.0 + 121.9	0.131	6.2	0.031
41 + 13	1464.5 + 121.9	0.310	6.3	0.070
42 + 9	1483.4 + 97.9	0.087	1.3	0.107
43 + 4	1519.5 + 54.2	0.112	6.4	0.037
43 + 8	1519.5 + 87.0	0.628	26.4	0.040

Amide I' mode of NMA-d_1/$(D_2O)_3$/PCM

(α,β)	ω	$\lvert C_{S\alpha\beta}\rvert$	$\lvert\Delta\omega\rvert$	$r_{S\alpha\beta}$
30 + 24	1046.9 + 581.4	4.028	39.0	0.080
34 + 20	1181.8 + 313.4	3.088	94.1	0.033
35 + 19	1189.8 + 307.6	3.537	91.8	0.039
36 + 21	1197.1 + 439.0	1.815	46.8	0.032
40 + 10	1446.8 + 110.5	3.002	32.0	0.142
41 + 11	1457.7 + 128.0	0.674	3.6	0.267
43 + 7	1522.4 + 63.0	0.074	3.9	0.037
43 + 8	1522.4 + 76.6	0.342	9.7	0.063

Amide I' mode of NMA-d_7

(α,β)	ω	$\lvert C_{S\alpha\beta}\rvert$	$\lvert\Delta\omega\rvert$	$r_{S\alpha\beta}$
10 + 10	801.0 + 801.0	6.254	63.1	0.073
12 + 12	898.8 + 898.8	6.722	132.6	0.033
13 + 9	932.8 + 731.5	2.357	0.8	2.222
15 + 10	1020.3 + 801.0	7.217	156.2	0.030
20 + 8	1111.8 + 563.3	2.650	9.9	0.200
22 + 4	1445.3 + 253.3	2.499	33.5	0.073

Amide I' mode of NMA-d_7/$(D_2O)_3$

(α,β)	ω	$\lvert C_{S\alpha\beta}\rvert$	$\lvert\Delta\omega\rvert$	$r_{S\alpha\beta}$
28 + 27	823.0 + 753.2	1.794	15.7	0.089
28 + 28	823.0 + 823.0	4.266	85.5	0.037
30 + 24	910.2 + 502.7	5.463	147.5	0.034
34 + 26	1043.3 + 580.3	2.663	63.1	0.033
35 + 24	1045.7 + 502.7	0.909	12.1	0.064
36 + 24	1052.7 + 502.7	0.367	5.0	0.062
38 + 21	1118.6 + 401.7	1.626	40.1	0.037
39 + 21	1181.0 + 401.7	2.625	22.3	0.105
41 + 19	1203.1 + 293.7	3.826	63.6	0.062
41 + 20	1203.1 + 310.1	1.736	47.2	0.037
41 + 21	1203.1 + 401.7	1.787	44.4	0.035
42 + 19	1217.4 + 293.7	1.758	49.3	0.037
42 + 20	1217.4 + 310.1	4.180	32.9	0.127
43 + 8	1499.6 + 84.0	0.678	23.2	0.050

Amide I' mode of NMA-d_7/$(D_2O)_3$/PCM

(α,β)	ω	$\lvert C_{S\alpha\beta}\rvert$	$\lvert\Delta\omega\rvert$	$r_{S\alpha\beta}$
27 + 27	755.6 + 755.6	1.953	51.1	0.031
28 + 27	827.5 + 755.6	2.220	20.7	0.083
30 + 24	910.4 + 532.4	4.701	119.6	0.035
30 + 26	910.4 + 601.7	2.646	50.4	0.043
34 + 24	1042.2 + 532.4	0.837	12.2	0.057
40 + 19	1182.1 + 303.4	4.326	76.9	0.058
41 + 21	1187.1 + 399.2	3.047	23.9	0.114
42 + 20	1191.4 + 308.1	4.753	62.9	0.076

Amide II' mode of NMA-d_1

(α,β)	ω	$\lvert C_{S\alpha\beta}\rvert$	$\lvert\Delta\omega\rvert$	$r_{S\alpha\beta}$
9 + 8	854.3 + 617.5	5.113	116.6	0.037
9 + 9	854.3 + 854.3	7.639	120.3	0.045
10 + 8	929.3 + 617.5	2.160	41.6	0.042
10 + 9	929.3 + 854.3	8.625	195.3	0.030
11 + 8	1001.1 + 617.5	3.455	30.2	0.088
21 + 1	1475.5 + 35.9	2.296	77.0	0.079

Amide II' mode of NMA-$d_1/(D_2O)_3$

(α,β)	ω	$\lvert C_{S\alpha\beta}\rvert$	$\lvert\Delta\omega\rvert$	$r_{S\alpha\beta}$
25 + 25	626.3 + 626.3	8.830	192.0	0.047
26 + 26	632.3 + 632.3	6.050	179.8	0.034
27 + 26	878.2 + 632.3	5.225	66.0	0.068
29 + 22	1015.9 + 443.6	2.213	15.0	0.140
30 + 1	1046.8 + 2.8	1.764	394.9	0.052
31 + 13	1132.2 + 121.9	4.115	190.4	0.037
32 + 18	1140.8 + 274.1	1.423	29.6	0.055
32 + 19	1140.8 + 302.7	1.330	1.0	1.438
32 + 20	1140.8 + 312.7	0.546	9.0	0.065
33 + 18	1186.4 + 274.1	0.458	16.0	0.032
34 + 18	1197.1 + 274.1	1.297	26.7	0.054
40 + 1	1452.0 + 2.8	0.051	10.3	0.049
41 + 1	1464.5 + 2.8	0.139	22.8	0.060

Amide II' mode of NMA-d_1/$(D_2O)_3$/PCM

(α,β)	ω	$\lvert C_{S\alpha\beta}\rvert$	$\lvert\Delta\omega\rvert$	$r_{S\alpha\beta}$
27 + 25	881.4 + 631.4	4.556	12.1	0.316
27 + 26	881.4 + 632.9	4.060	13.6	0.249
29 + 21	1020.5 + 439.0	1.399	41.2	0.032
34 + 19	1181.8 + 307.6	1.150	11.3	0.105
34 + 20	1181.8 + 313.4	0.380	5.5	0.071
35 + 19	1189.8 + 307.6	0.455	3.3	0.144
35 + 20	1189.8 + 313.4	0.214	2.5	0.087
36 + 18	1197.1 + 277.9	1.225	25.7	0.052
36 + 19	1197.1 + 307.6	0.754	4.0	0.194
36 + 20	1197.1 + 313.4	1.279	9.8	0.133
38 + 8	1423.3 + 76.6	0.131	0.8	0.315
41 + 4	1457.7 + 39.8	0.083	3.2	0.067
41 + 11	1457.7 + 128.0	2.212	85.0	0.038

Amide II' mode of NMA-d_7

(α,β)	ω	$\lvert C_{S\alpha\beta}\rvert$	$\lvert\Delta\omega\rvert$	$r_{S\alpha\beta}$
9 + 9	731.5 + 731.5	5.060	35.4	0.125
10 + 8	801.0 + 563.3	3.489	63.3	0.053
10 + 9	801.0 + 731.5	5.113	104.9	0.041
11 + 7	883.2 + 536.0	0.722	8.5	0.079
12 + 7	898.8 + 536.0	1.799	7.1	0.232
19 + 5	1063.0 + 339.3	0.784	25.4	0.033
21 + 4	1172.0 + 253.3	2.738	2.4	1.366

Amide II' mode of NMA-d_7/$(D_2O)_3$

(α,β)	ω	$\lvert C_{S\alpha\beta}\rvert$	$\lvert\Delta\omega\rvert$	$r_{S\alpha\beta}$
28 + 26	823.0 + 580.3	3.838	4.0	0.886
29 + 24	883.3 + 502.7	3.923	21.3	0.178
30 + 24	910.2 + 502.7	2.487	5.6	0.420
30 + 25	910.2 + 559.9	3.308	62.9	0.048
31 + 21	954.0 + 401.7	1.640	51.5	0.033
32 + 21	1021.7 + 401.7	1.103	16.2	0.069
39 + 18	1181.0 + 255.2	2.197	28.9	0.089

Amide II' mode of NMA-d_7/$(D_2O)_3$/PCM

(α,β)	ω	$\lvert C_{S\alpha\beta}\rvert$	$\lvert\Delta\omega\rvert$	$r_{S\alpha\beta}$
27 + 27	755.6 + 755.6	1.473	22.7	0.054
28 + 25	827.5 + 580.0	3.842	81.1	0.043
28 + 27	827.5 + 755.6	3.838	94.6	0.032
29 + 24	884.3 + 532.4	2.950	71.9	0.038
29 + 26	884.3 + 601.7	2.916	2.6	0.959
30 + 24	910.4 + 532.4	4.605	45.8	0.091
30 + 26	910.4 + 601.7	1.483	23.5	0.053
40 + 19	1182.1 + 303.4	0.232	3.0	0.081
40 + 20	1182.1 + 308.1	0.908	1.6	0.576
41 + 18	1187.1 + 259.0	1.895	42.5	0.051
41 + 19	1187.1 + 303.4	1.205	2.0	0.644
42 + 19	1191.4 + 303.4	0.775	6.3	0.128