Supporting Information

An Inversion-Recovery NMR Kinetics Experiment

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Contents

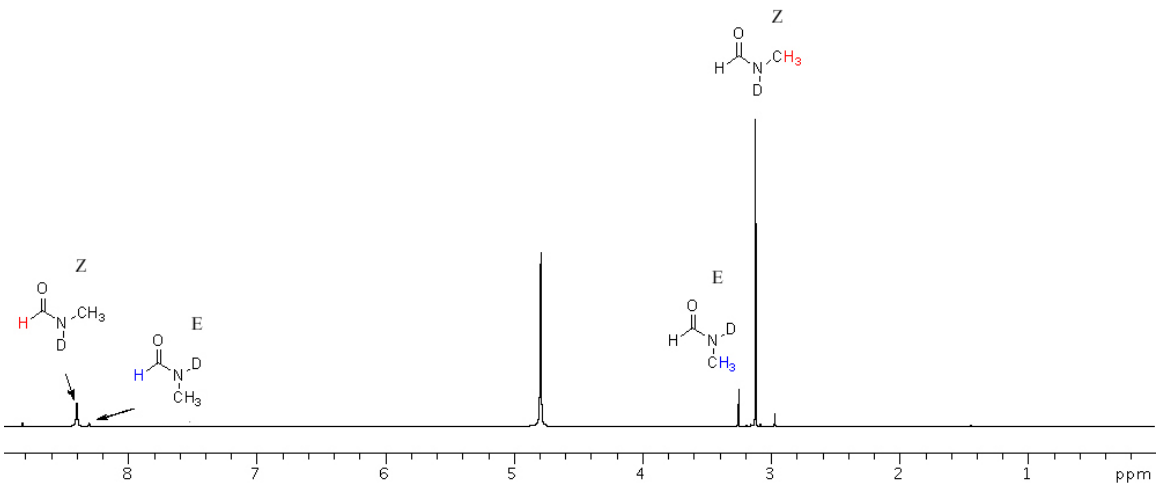
I. General Procedures

Water-d_2 was purchased from Cambridge Isotopes Labs; *N*-methylformamide was purchased from Alfa Aesar. Both were used as received. Samples were prepared in Wilmad 535-PP NMR tubes sealed with plastic caps and parafilm. These were stored on the benchtop with minimal degradation for a period of days. NMR spectra were obtained on a Varian NMRS 500 spectrometer. All chemical shifts are reported in units of ppm and referenced to the residual HOD. Temperature was calibrated using an ethylene glycol standard.

II. Raw NMR Data and CIFIT Fit Data

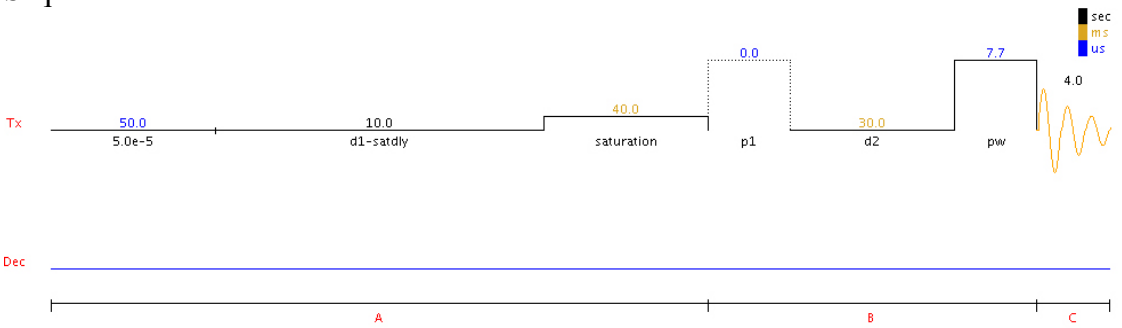
II.A. Steady-State Spectra and Pulse Sequence

Figure S1. Labeled ^{1}H Spectrum of *N*-Methylformamide-*N*-d_1.



Spectrum was acquired in water-d_2 at 60.30 °C at 500 MHz. Methylamine-d_2 (3 ppm) and formate-*d* (8.8 ppm) resulting from slow hydrolysis of *N*-methylformamide can be seen in this spectrum. In our hands, samples are good for about two weeks of use before these hydrolysis products become an issue. This particular sample had been in use in our class for over 1 week.

Figure S2. Varian's PRESAT Pulse Sequence.



PRESAT pulse sequence as configured for the acquisition of data presented in Figure S3. Parameters: d1 = 10 s (recycle delay); satdly = 40 ms (inversion pulse width); p1 = 0 (this pulse is off), d2 = (arrayed) (interpulse delay); pw = 7.7 μs (detection pulse width); at = 4 s (acquisition time); satpwr = -7 (inversion pulse power) (14 Hz width); tpwr = 61 (detection pulse power).

II.B. 60 °C

Figure S3. Stacked Spectra.

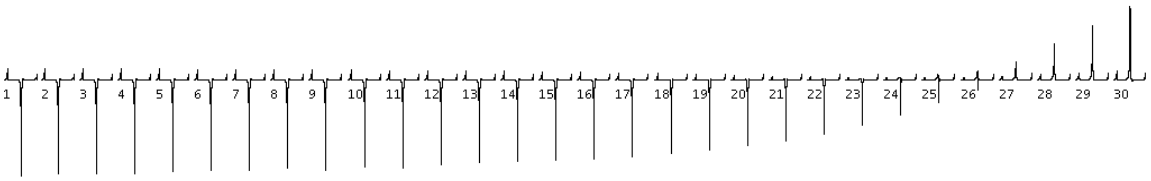
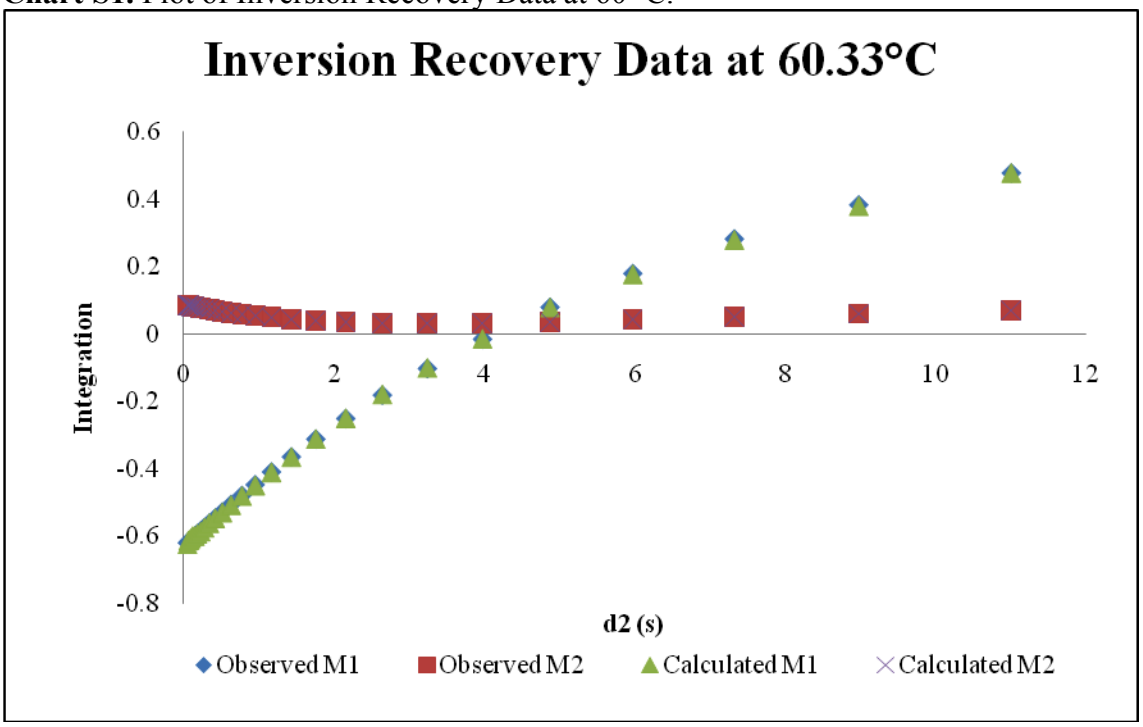


Table S1. CIFIT Plot File.

d2 (s)	Observed M1	Observed M2	Fit M1	Fit M2	σM1	σM2
0.0553	-0.6193	0.0843	-0.6237	0.0844	0.0044	-0.0001
0.0677	-0.6168	0.0838	-0.6128	0.0842	-0.004	-0.0004
0.0830	-0.6136	0.0831	-0.6109	0.0834	-0.0027	-0.0003
0.1018	-0.6098	0.0822	-0.6059	0.0815	-0.0039	0.0008
0.1248	-0.6051	0.0812	-0.5995	0.0815	-0.0056	-0.0003
0.1529	-0.5994	0.0800	-0.5996	0.0798	0.0002	0.0002
0.1875	-0.5924	0.0785	-0.5927	0.0784	0.0003	0.0001
0.2298	-0.5839	0.0768	-0.5863	0.0772	0.0024	-0.0004
0.2817	-0.5735	0.0747	-0.5745	0.0743	0.001	0.0004
0.3453	-0.5610	0.0723	-0.5612	0.0724	0.0002	-0.0001
0.4233	-0.5457	0.0694	-0.5467	0.0695	0.001	-0.0002
0.5189	-0.5273	0.0661	-0.5298	0.0661	0.0025	0
0.636	-0.5051	0.0623	-0.5079	0.0623	0.0027	0
0.7796	-0.4785	0.0581	-0.4806	0.0581	0.0022	0
0.9557	-0.4466	0.0535	-0.4495	0.0533	0.0029	0.0001
1.1710	-0.4088	0.0486	-0.4103	0.0484	0.0016	0.0002
1.4360	-0.3639	0.0437	-0.3649	0.0435	0.001	0.0001
1.7600	-0.3115	0.0390	-0.3109	0.039	-0.0006	0
2.1580	-0.2506	0.0349	-0.2493	0.035	-0.0013	0
2.6450	-0.1810	0.0320	-0.1786	0.0319	-0.0024	0.0001
3.2423	-0.1023	0.0308	-0.0994	0.0309	-0.0029	-0.0001
3.9745	-0.0150	0.0318	-0.0131	0.0319	-0.0019	-0.0001
4.8719	0.0797	0.0353	0.0798	0.0354	-0.0001	-0.0001
5.9720	0.1798	0.0414	0.1784	0.0414	0.0015	0
7.3206	0.2823	0.0498	0.2806	0.0498	0.0018	-0.0001
8.9740	0.3832	0.0596	0.3815	0.0594	0.0017	0.0002
11.0000	0.4778	0.0700	0.4797	0.0701	-0.0019	-0.0001

Chart S1. Plot of Inversion Recovery Data at 60 °C.



CIFIT Guesses and Fit Parameters

Initial values of parameters:

1/T1's

No. 0= 0.3500 No. 1= 0.3500

M(inf)'s

No. 2= 0.4900 No. 3= 0.0700

M(0)-M(inf)'s

No. 4= -1.1137 No. 5= 0.0140

and M(0)'s for reference

No. 4= -0.6237 No. 5= 0.0840

Rates

No. 6= 0.0200

Final Values of Fitted Parameters and Uncertainties:

#	0 =	0.110790 +/-	0.001454
#	1 =	0.425066 +/-	0.035249
#	2 =	0.752979 +/-	0.004864
#	3 =	0.103367 +/-	0.004704
#	4 =	-1.383735 +/-	0.004659
#	5 =	-0.016461 +/-	0.005013
#	6 =	0.039760 +/-	0.001229

II.C. 65 °C

Figure S4. Stacked Spectra.

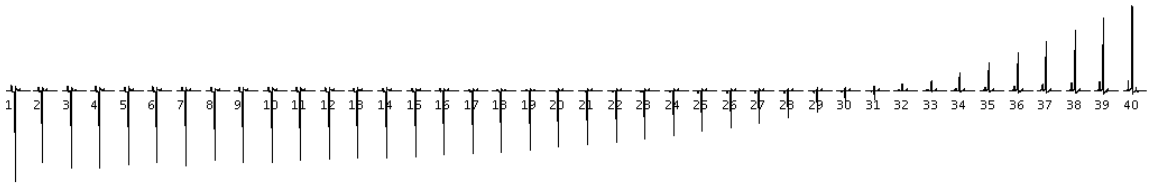
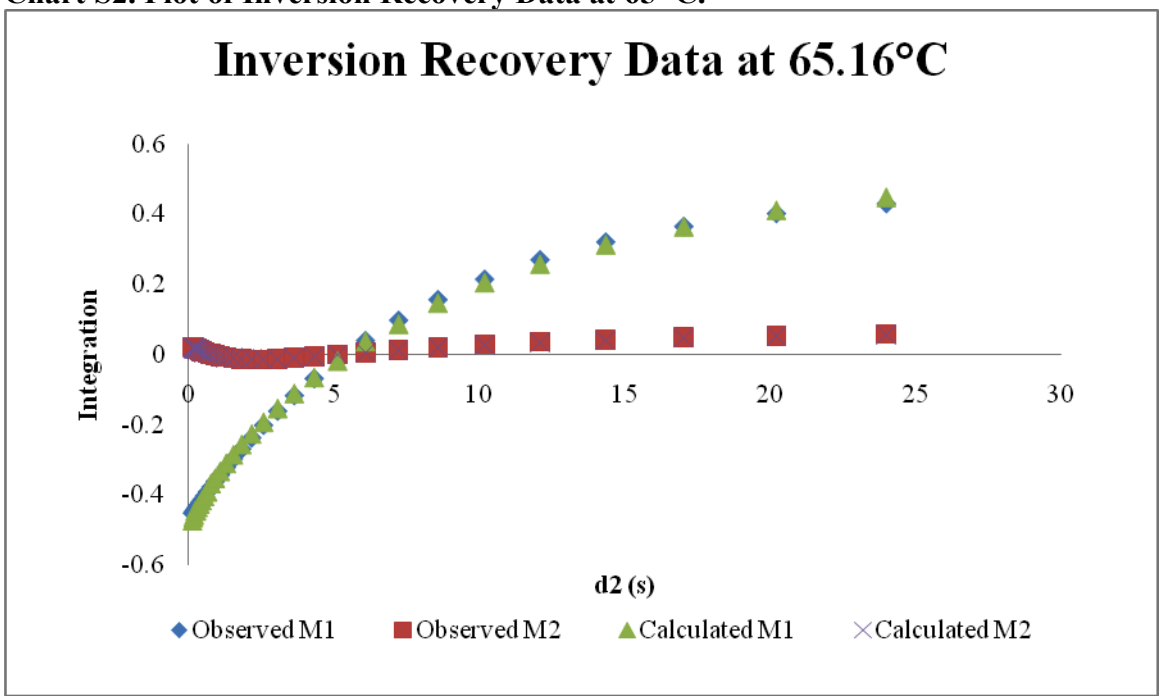


Table S2. CIFIT Plot File.

d2 (s)	Observed M1	Observed M2	Fit M1	Fit M2	σM1	σM2
0.1403	-0.4536	0.0206	-0.4748	0.0182	0.0212	0.0024
0.1665	-0.4504	0.0195	-0.465	0.0186	0.0146	0.0009
0.1977	-0.4466	0.0181	-0.458	0.0157	0.0115	0.0024
0.2346	-0.4421	0.0166	-0.4457	0.0152	0.0036	0.0014
0.2785	-0.4368	0.0148	-0.446	0.0145	0.0092	0.0003
0.3306	-0.4306	0.0128	-0.4358	0.0119	0.0053	0.0009
0.3924	-0.4232	0.0105	-0.4264	0.0114	0.0032	-0.0008
0.4657	-0.4146	0.0080	-0.4165	0.0077	0.0018	0.0003
0.5528	-0.4045	0.0053	-0.4049	0.0054	0.0004	-0.0002
0.65626	-0.3927	0.0023	-0.3918	0.0028	-0.0009	-0.0005
0.7788	-0.3789	-0.0008	-0.3684	-0.0011	-0.0105	0.0003
0.9245	-0.3629	-0.0040	-0.3534	-0.0038	-0.0095	-0.0002
1.0973	-0.3444	-0.0071	-0.3337	-0.0065	-0.0107	-0.0007
1.3025	-0.3230	-0.0101	-0.3108	-0.0094	-0.0122	-0.0007
1.5460	-0.2984	-0.0127	-0.2861	-0.0113	-0.0123	-0.0013
1.8350	-0.2702	-0.0146	-0.2569	-0.0132	-0.0134	-0.0014
2.1781	-0.2383	-0.0158	-0.227	-0.0141	-0.0113	-0.0016
2.5853	-0.2023	-0.0158	-0.1933	-0.0133	-0.009	-0.0025
3.0687	-0.1620	-0.0146	-0.154	-0.0126	-0.008	-0.002
3.6424	-0.1175	-0.0119	-0.1115	-0.01	-0.0059	-0.002
4.3234	-0.0687	-0.0079	-0.0659	-0.006	-0.0028	-0.0019
5.1318	-0.0161	-0.0025	-0.0188	-0.0011	0.0028	-0.0014
6.0912	0.0398	0.0039	0.037	0.0055	0.0028	-0.0015
7.2301	0.0979	0.0112	0.0864	0.0111	0.0115	0.0001
8.5819	0.1569	0.0190	0.1467	0.0186	0.0102	0.0003
10.1860	0.2152	0.0268	0.205	0.0255	0.0102	0.0012
12.0909	0.2708	0.0343	0.2578	0.0322	0.013	0.0021
14.3515	0.3218	0.0412	0.3131	0.0387	0.0087	0.0025
17.0347	0.3662	0.0473	0.3643	0.0459	0.0019	0.0014
20.2196	0.4030	0.0523	0.4112	0.0514	-0.0082	0.0009
24.0000	0.4313	0.0561	0.4484	0.0556	-0.0171	0.0005

Chart S2. Plot of Inversion Recovery Data at 65 °C.



CIFIT Guesses and Fit Parameters
Initial values of parameters:
1/T1's
No. 0= 0.4500 No. 1= 0.4500
M(inf)'s
No. 2= 0.4500 No. 3= 0.0570
M(0)-M(inf)'s
No. 4= -0.9200 No. 5= -0.0070
and M(0)'s for reference
No. 4= -0.4700 No. 5= 0.0500
Rates
No. 6= 0.0500
Chi squared value = 1.98601777

Final Values of Fitted Parameters and Uncertainties:

#	0 =	0.055007 +/-	0.012862
#	1 =	0.636309 +/-	0.140267
#	2 =	0.478247 +/-	0.007042
#	3 =	0.062537 +/-	0.004731
#	4 =	-0.949328 +/-	0.006586
#	5 =	-0.035127 +/-	0.007219
#	6 =	0.080660 +/-	0.013988

II.D. 75 °C

Figure S5. Stacked Spectra.

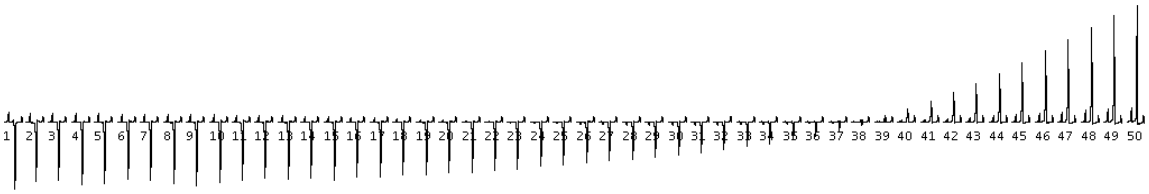
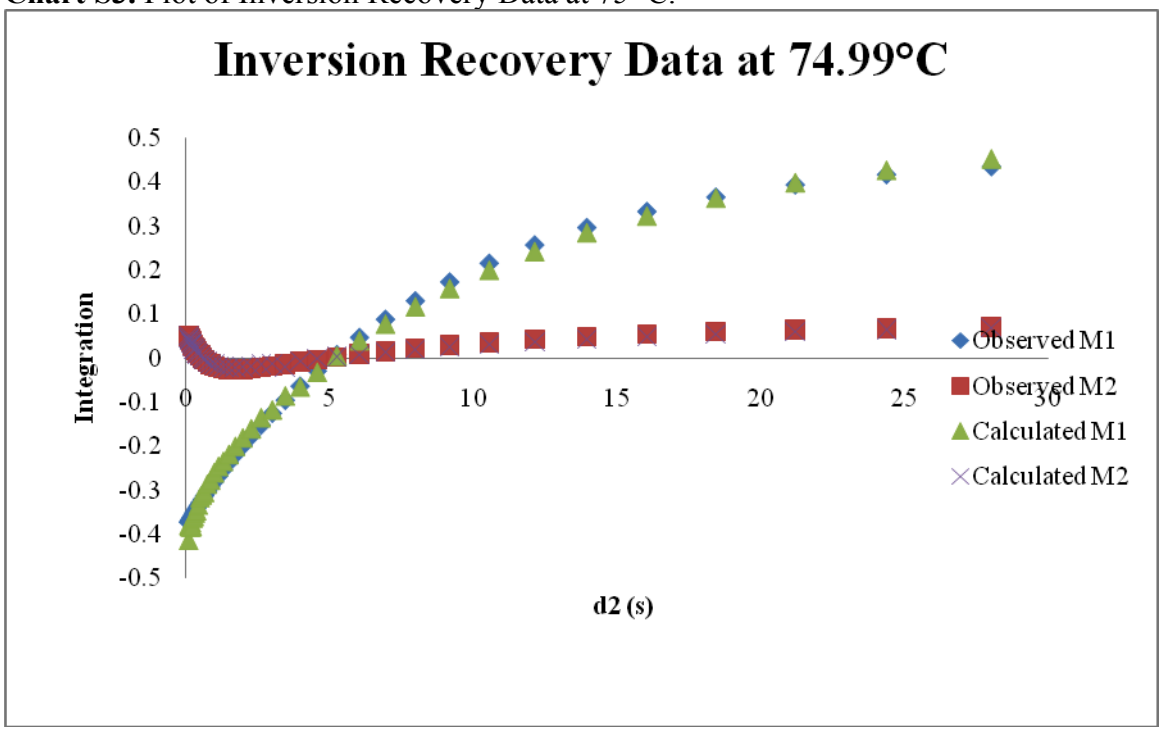


Table S3. CIFIT Plot File.

d2 (s)	Observed M1	Observed M2	Fit M1	Fit M2	σM1	σM2
0.0916	-0.3733	0.0498	-0.415	0.0519	0.0417	-0.0021
0.1054	-0.3717	0.0477	-0.3805	0.0455	0.0089	0.0022
0.1211	-0.3698	0.0452	-0.3833	0.0431	0.0135	0.0021
0.1393	-0.3676	0.0425	-0.3824	0.0399	0.0148	0.0026
0.1601	-0.3652	0.0395	-0.3846	0.0343	0.0194	0.0053
0.1841	-0.3624	0.0362	-0.3748	0.0328	0.0125	0.0034
0.2117	-0.3592	0.0326	-0.3837	0.0309	0.0245	0.0017
0.2434	-0.3556	0.0286	-0.3641	0.0255	0.0086	0.0031
0.2799	-0.3515	0.0243	-0.3604	0.0202	0.0089	0.0041
0.32177	-0.3468	0.0197	-0.3525	0.0191	0.0057	0.0005
0.3700	-0.3416	0.0148	-0.3478	0.0114	0.0062	0.0034
0.4254	-0.3357	0.0097	-0.3347	0.008	-0.001	0.0017
0.4891	-0.3290	0.0045	-0.3175	0.0032	-0.0115	0.0013
0.5623	-0.3215	-0.0008	-0.3115	-0.001	-0.0101	0.0002
0.6466	-0.3131	-0.006	-0.3059	-0.0047	-0.0072	-0.0014
0.7434	-0.3037	-0.011	-0.2872	-0.0094	-0.0165	-0.0017
0.8547	-0.2931	-0.0157	-0.2782	-0.0128	-0.015	-0.0029
0.9828	-0.2814	-0.0198	-0.2613	-0.0151	-0.0201	-0.0047
1.1300	-0.2682	-0.0232	-0.2467	-0.019	-0.0215	-0.0042
1.2992	-0.2536	-0.0258	-0.2353	-0.0207	-0.0183	-0.005
1.4938	-0.2374	-0.0273	-0.2194	-0.0217	-0.0179	-0.0056
1.7175	-0.2193	-0.0279	-0.2011	-0.022	-0.0182	-0.0059
1.9747	-0.1993	-0.0273	-0.1818	-0.0208	-0.0174	-0.0066
2.2705	-0.1771	-0.0258	-0.1611	-0.0201	-0.016	-0.0056
2.6106	-0.1526	-0.0232	-0.1358	-0.0153	-0.0168	-0.0079
3.0016	-0.1258	-0.0197	-0.1181	-0.0135	-0.0077	-0.0062
3.4511	-0.0963	-0.0155	-0.0862	-0.0206	-0.0102	0.0051
3.9680	-0.0643	-0.0106	-0.066	-0.0082	0.0017	-0.0024
4.5624	-0.0298	-0.0052	-0.0324	-0.0027	0.0026	-0.0024
5.2457	0.0072	0.0007	0.0046	0.0029	0.0026	-0.0022
6.0314	0.0463	0.007	0.0396	0.0078	0.0067	-0.0008
6.9347	0.0872	0.0136	0.0772	0.0136	0.01	0
7.9734	0.1294	0.0204	0.1169	0.0188	0.0124	0.0016
9.1676	0.1721	0.0273	0.1584	0.0247	0.0138	0.0026
10.5406	0.2147	0.0342	0.1997	0.0311	0.015	0.003
12.1194	0.2562	0.0408	0.2424	0.0373	0.0139	0.0036
13.9345	0.2957	0.0472	0.2855	0.0429	0.0102	0.0043
16.0216	0.3321	0.0531	0.3231	0.0487	0.009	0.0043
18.4212	0.3647	0.0583	0.3639	0.0536	0.0008	0.0047
21.1803	0.3928	0.0628	0.3993	0.0595	-0.0066	0.0034
24.3526	0.4159	0.0666	0.4277	0.0644	-0.0118	0.0022
28.0000	0.4341	0.0695	0.4535	0.0684	-0.0194	0.0011

Chart S3. Plot of Inversion Recovery Data at 75 °C.



CIFIT Guesses and Fit Parameters
Initial values of parameters:
1/T1's
No. 0= 0.4500 No. 1= 0.4500
M(inf)'s
No. 2= 0.4500 No. 3= 0.0750
M(0)-M(inf)'s
No. 4= -0.8800 No. 5= -0.0150
and M(0)'s for reference
No. 4= -0.4300 No. 5= 0.0600
Rates
No. 6= 0.1400
Chi squared value = 2.36712697

Final Values of Fitted Parameters and Uncertainties:

# 0 =	-0.086725	+/-	0.028207
# 1 =	1.348414	+/-	0.230371
# 2 =	0.469951	+/-	0.008874
# 3 =	0.075276	+/-	0.005171
# 4 =	-0.854623	+/-	0.008460
# 5 =	-0.009554	+/-	0.009552
# 6 =	0.237355	+/-	0.032392

II.E. 82 °C

Figure S6. Stacked Spectra.

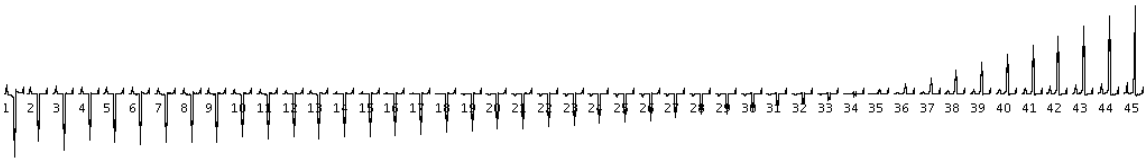
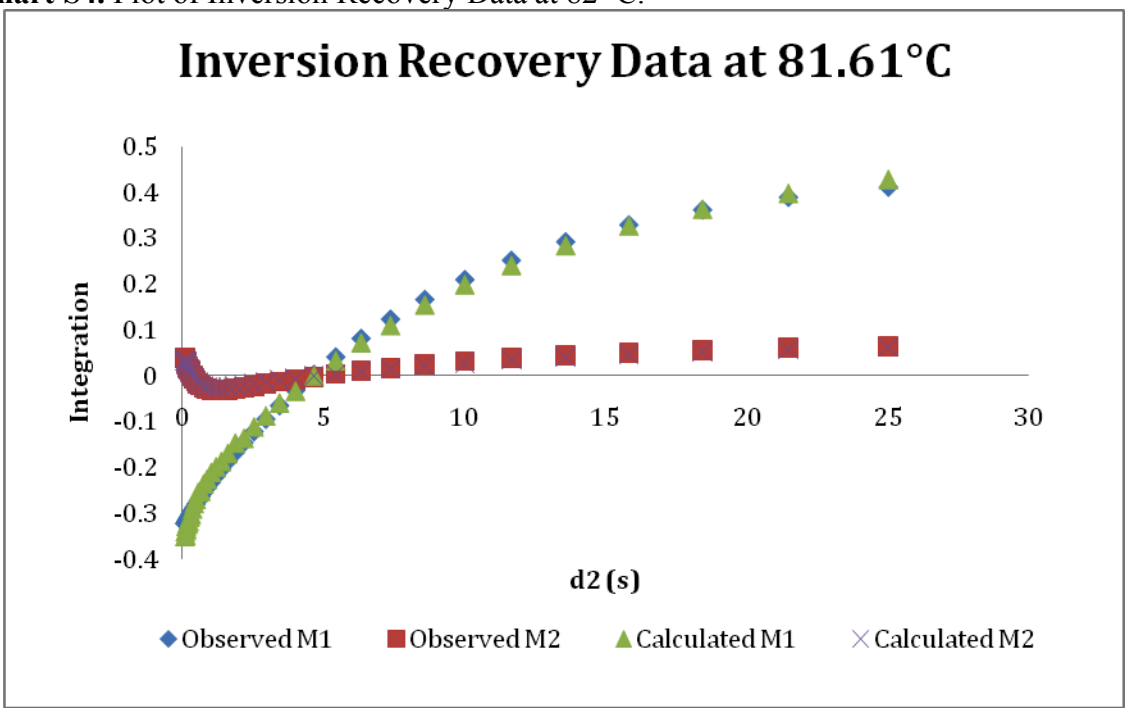


Table S4. CIFIT Plot File.

d2 (s)	Observed M1	Observed M2	Fit M1	Fit M2	σM1	σM2
0.0751	-0.3227	0.0391	-0.3515	0.0364	0.0288	0.0028
0.0875	-0.3212	0.0366	-0.3409	0.0312	0.0197	0.0054
0.1019	-0.3195	0.0338	-0.349	0.0317	0.0295	0.0021
0.1187	-0.3174	0.0306	-0.3287	0.0295	0.0113	0.001
0.1383	-0.3151	0.0270	-0.3359	0.0246	0.0208	0.0025
0.1612	-0.3125	0.0231	-0.322	0.0208	0.0095	0.0024
0.1878	-0.3095	0.0189	-0.3241	0.0154	0.0147	0.0035
0.2188	-0.3060	0.0143	-0.3185	0.0113	0.0125	0.003
0.2550	-0.3020	0.0094	-0.3083	0.0073	0.0063	0.0021
0.2971	-0.2975	0.0042	-0.303	0.003	0.0055	0.0012
0.3461	-0.2924	-0.0011	-0.2911	-0.0023	-0.0013	0.0012
0.4033	-0.2866	-0.0065	-0.2789	-0.0066	-0.0077	0.0001
0.4699	-0.2800	-0.0117	-0.2699	-0.0113	-0.0102	-0.0004
0.5475	-0.2726	-0.0167	-0.2548	-0.0157	-0.0178	-0.001
0.6379	-0.2643	-0.0213	-0.2521	-0.0188	-0.0122	-0.0025
0.7433	-0.2549	-0.0252	-0.2364	-0.0218	-0.0185	-0.0034
0.8660	-0.2443	-0.0283	-0.2262	-0.025	-0.018	-0.0033
1.0091	-0.2323	-0.0305	-0.2114	-0.0251	-0.0209	-0.0054
1.1757	-0.2189	-0.0316	-0.1993	-0.026	-0.0196	-0.0056
1.3699	-0.2037	-0.0316	-0.1876	-0.0271	-0.0161	-0.0045
1.5961	-0.1867	-0.0306	-0.1699	-0.0246	-0.0168	-0.0061
1.8597	-0.1675	-0.0287	-0.1472	-0.0215	-0.0203	-0.0072
2.1668	-0.1459	-0.0259	-0.1371	-0.0211	-0.0088	-0.0047
2.5247	-0.1218	-0.0224	-0.112	-0.0173	-0.0098	-0.005
2.9416	-0.0949	-0.0182	-0.0879	-0.014	-0.007	-0.0043
3.4275	-0.0652	-0.0135	-0.0596	-0.01	-0.0056	-0.0036
3.9935	-0.0326	-0.0083	-0.0339	-0.0061	0.0012	-0.0022
4.6530	0.0028	-0.0026	-0.0002	-0.0013	0.003	-0.0013
5.4215	0.0408	0.0035	0.0325	0.0036	0.0083	-0.0002
6.3168	0.0811	0.0100	0.072	0.0093	0.009	0.0006
7.3601	0.1231	0.0167	0.1092	0.0149	0.0139	0.0018
8.5756	0.1661	0.0236	0.1544	0.0211	0.0117	0.0026
9.9919	0.2093	0.0306	0.1984	0.0273	0.0109	0.0033
11.6420	0.2515	0.0374	0.2407	0.0337	0.0108	0.0036
13.5647	0.2917	0.0438	0.2841	0.0398	0.0076	0.004
15.8050	0.3286	0.0497	0.3269	0.0455	0.0017	0.0042
18.4152	0.3613	0.0550	0.3633	0.0518	-0.002	0.0032
21.4564	0.3888	0.0594	0.3979	0.056	-0.0091	0.0034
25.0000	0.4109	0.0630	0.4282	0.0616	-0.0173	0.0013

Chart S4. Plot of Inversion Recovery Data at 82 °C.



CIFIT Guesses and Fit Parameters
Initial values of parameters:
1/T1's
No. 0= 0.5500 No. 1= 0.5500
M(inf)'s
No. 2= 0.4400 No. 3= 0.0630
M(0)-M(inf)'s
No. 4= -0.8400 No. 5= 0.0230
and M(0)'s for reference
No. 4= -0.4000 No. 5= 0.0860
Rates
No. 6= 0.3810

Final Values of Fitted Parameters and Uncertainties:

#	0 =	-0.187575 +/-	0.049106
#	1 =	1.992622 +/-	0.380015
#	2 =	0.455230 +/-	0.010050
#	3 =	0.070076 +/-	0.005332
#	4 =	-0.787438 +/-	0.009574
#	5 =	-0.013841 +/-	0.010461
#	6 =	0.359539 +/-	0.056910

II.F. 89 °C

Figure S7. Stacked Spectra.

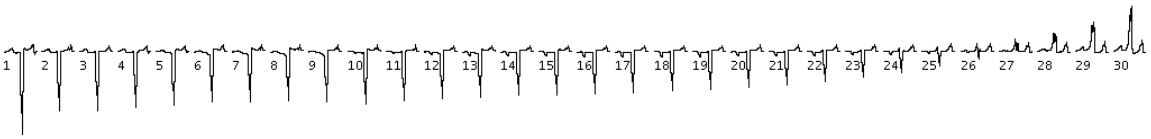
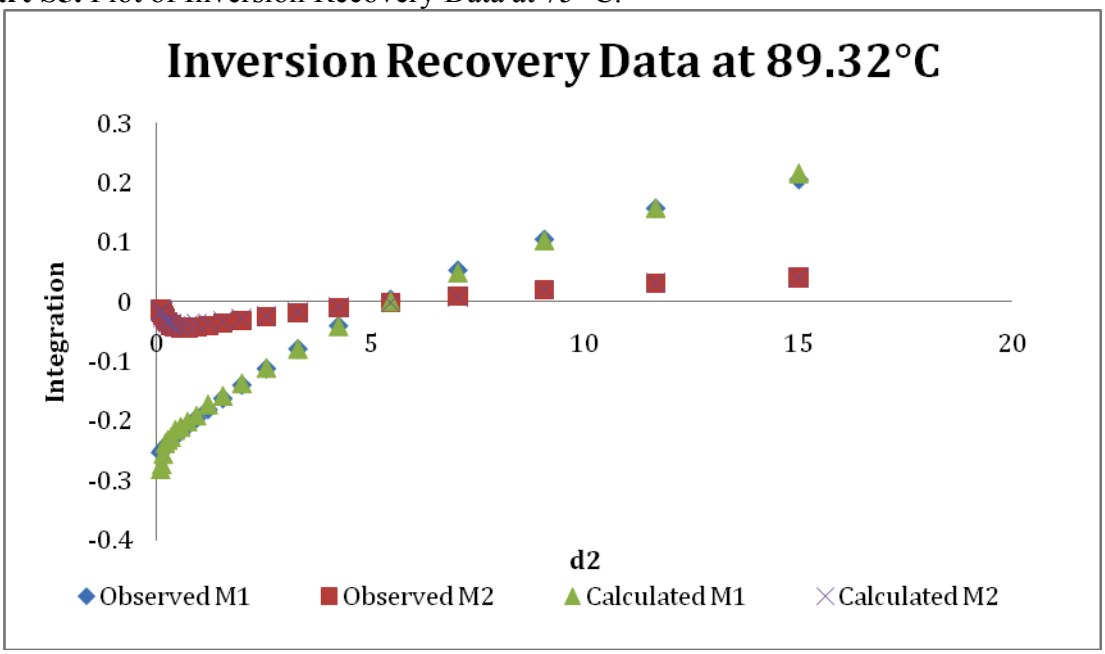


Table S5. CIFIT Plot File.

d2 (s)	Observed M1	Observed M2	Fit M1	Fit M2	σM1	σM2
0.0968	-0.2535	-0.0132	-0.2809	-0.015	0.0275	0.0018
0.1245	-0.2507	-0.0181	-0.2727	-0.0149	0.022	-0.0032
0.1602	-0.2473	-0.0235	-0.2551	-0.0259	0.0078	0.0024
0.2062	-0.2432	-0.029	-0.2371	-0.0329	-0.0061	0.0039
0.2653	-0.2384	-0.0342	-0.2316	-0.0346	-0.0067	0.0004
0.3414	-0.2326	-0.0388	-0.227	-0.0363	-0.0056	-0.0024
0.4393	-0.2258	-0.0421	-0.215	-0.0405	-0.0108	-0.0017
0.5654	-0.2177	-0.044	-0.2098	-0.0408	-0.0079	-0.0032
0.7275	-0.2079	-0.0441	-0.2006	-0.0387	-0.0073	-0.0055
0.9362	-0.1959	-0.0427	-0.1907	-0.0366	-0.0052	-0.0061
1.2047	-0.1809	-0.04	-0.1721	-0.0352	-0.0089	-0.0049
1.5503	-0.1625	-0.0363	-0.1576	-0.0322	-0.0049	-0.0041
1.9949	-0.1397	-0.0315	-0.1366	-0.0284	-0.0031	-0.0032
2.5671	-0.1121	-0.0257	-0.1107	-0.0227	-0.0014	-0.003
3.3035	-0.0789	-0.0188	-0.079	-0.0162	0.0001	-0.0025
4.2510	-0.0400	-0.0106	-0.0411	-0.0089	0.0011	-0.0017
5.4703	0.0045	-0.0013	0.0005	-0.0007	0.004	-0.0006
7.0393	0.0536	0.009	0.049	0.0089	0.0046	0.0001
9.0584	0.1056	0.02	0.1032	0.0204	0.0025	-0.0004
11.657	0.1577	0.0309	0.1573	0.0314	0.0004	-0.0005
15.0000	0.2061	0.0411	0.2156	0.041	-0.0094	0

Chart S5. Plot of Inversion Recovery Data at 75 °C.



CIFIT Guesses and Fit Parameters
Initial values of parameters:
1/T1's
No. 0= 0.5500 No. 1= 0.5500
M(inf)'s
No. 2= 0.2500 No. 3= 0.0450
M(0)-M(inf)'s
No. 4= -0.5500 No. 5= -0.0450
and M(0)'s for reference
No. 4= -0.3000 No. 5= 0.0000
Rates
No. 6= 0.4500
Chi squared value = 0.65220288

Final Values of Fitted Parameters and Uncertainties:

# 0 =	-0.675572	+/-	0.292120
# 1 =	3.849183	+/-	1.533854
# 2 =	0.315771	+/-	0.020423
# 3 =	0.064079	+/-	0.007623
# 4 =	-0.580577	+/-	0.019712
# 5 =	-0.053012	+/-	0.020954
# 6 =	0.993697	+/-	0.362123

II.F.103 °C

Figure S8. Stacked Spectra.

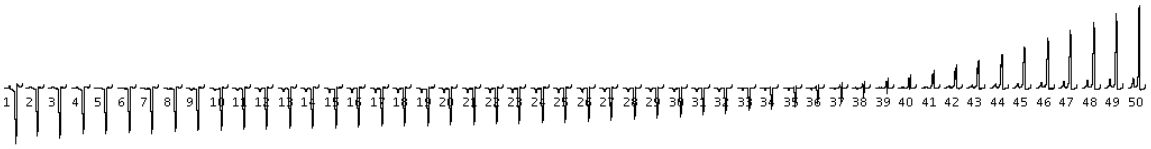
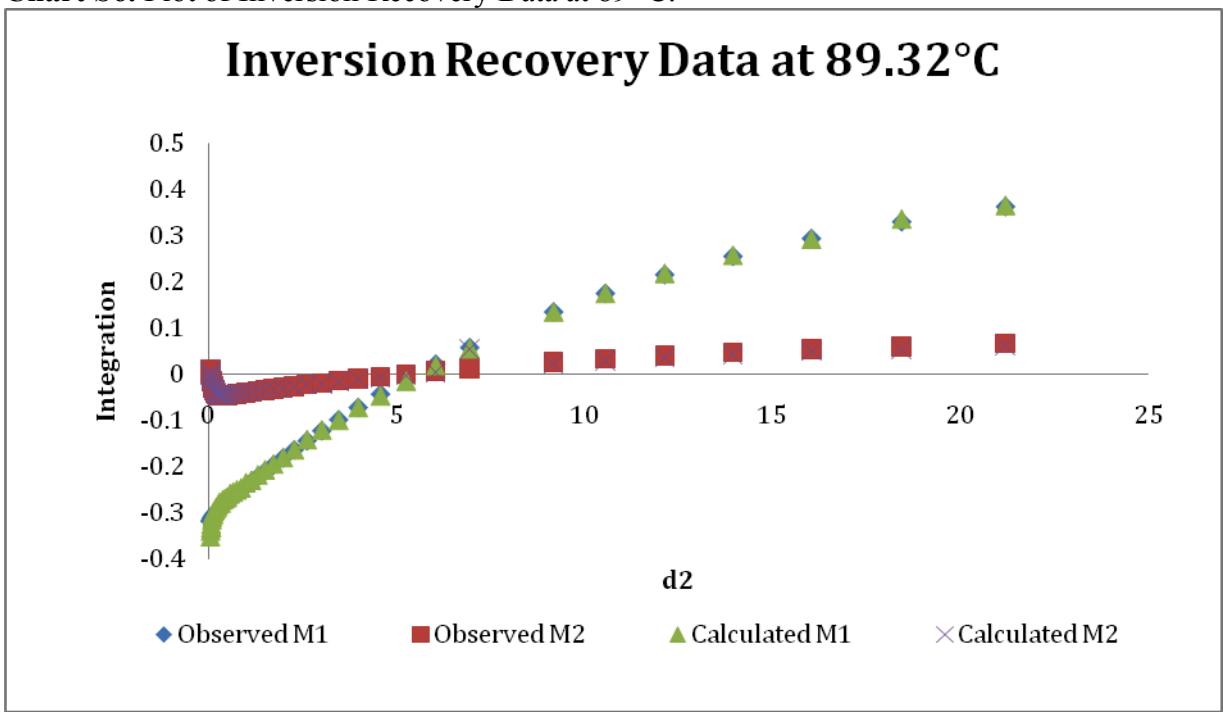


Table S6. CIFIT Plot File.

d2 (s)	Observed M1	Observed M2	Fit M1	Fit M2	σM1	σM2
0.0397	-0.3181	0.0115	-0.3531	0.0089	0.0349	0.0025
0.0456	-0.3168	0.0064	-0.3403	0.0005	0.0235	0.0059
0.0524	-0.3154	0.0010	-0.3336	-0.0024	0.0182	0.0034
0.0603	-0.3138	-0.0045	-0.3254	-0.0062	0.0116	0.0017
0.0693	-0.3122	-0.0101	-0.3325	-0.0133	0.0203	0.0032
0.0797	-0.3104	-0.0157	-0.3159	-0.0159	0.0055	0.0002
0.0916	-0.3086	-0.0212	-0.3099	-0.0211	0.0013	0
0.1054	-0.3067	-0.0263	-0.3025	-0.0283	-0.0041	0.0019
0.1211	-0.3047	-0.0311	-0.3044	-0.0301	-0.0002	-0.001
0.1393	-0.3026	-0.0353	-0.2977	-0.0339	-0.0049	-0.0014
0.1601	-0.3005	-0.0390	-0.2945	-0.0361	-0.006	-0.0028
0.1841	-0.2982	-0.0419	-0.2911	-0.0405	-0.0071	-0.0014
0.2117	-0.2958	-0.0441	-0.2895	-0.0436	-0.0063	-0.0005
0.2434	-0.2933	-0.0456	-0.2846	-0.0444	-0.0086	-0.0013
0.2799	-0.2905	-0.0465	-0.2787	-0.0448	-0.0118	-0.0017
0.3218	-0.2874	-0.0469	-0.2796	-0.0454	-0.0078	-0.0015
0.3700	-0.284	-0.0468	-0.273	-0.0463	-0.0109	-0.0006
0.4254	-0.2801	-0.0465	-0.2702	-0.0455	-0.0099	-0.001
0.4891	-0.2757	-0.0458	-0.2669	-0.045	-0.0088	-0.0008
0.5623	-0.2707	-0.0450	-0.2594	-0.0447	-0.0113	-0.0003
0.6466	-0.265	-0.0440	-0.2559	-0.0431	-0.0091	-0.0009
0.7434	-0.2585	-0.0429	-0.2515	-0.0419	-0.007	-0.001
0.8547	-0.2511	-0.0416	-0.247	-0.0408	-0.0041	-0.0008
0.9828	-0.2427	-0.0401	-0.2359	-0.0389	-0.0067	-0.0012
1.1300	-0.2331	-0.0384	-0.2303	-0.0381	-0.0028	-0.0003
1.2992	-0.2223	-0.0365	-0.2187	-0.0363	-0.0036	-0.0002
1.4938	-0.2100	-0.0344	-0.2078	-0.0347	-0.0022	0.0004
1.7175	-0.1962	-0.0319	-0.195	-0.0337	-0.0012	0.0018
1.9747	-0.1806	-0.0292	-0.1809	-0.0299	0.0003	0.0007
2.2705	-0.1632	-0.0261	-0.164	-0.0273	0.0008	0.0012
2.6106	-0.1437	-0.0227	-0.142	-0.022	-0.0017	-0.0007
3.0016	-0.1220	-0.0189	-0.1214	-0.02	-0.0006	0.0012
3.4511	-0.0980	-0.0146	-0.1003	-0.0162	0.0023	0.0016
3.9680	-0.0716	-0.0100	-0.0723	-0.0109	0.0007	0.0009
4.5624	-0.0427	-0.0049	-0.0471	-0.0073	0.0044	0.0024
5.2457	-0.0114	0.0006	-0.0155	-0.0016	0.0041	0.0022
6.0314	0.0223	0.0066	0.0184	0.0041	0.0039	0.0025
6.9347	0.0582	0.0129	0.0551	0.0551	0.0032	-0.0422
9.1676	0.1353	0.0265	0.1347	0.0229	0.0007	0.0036
10.5406	0.1755	0.0336	0.1751	0.0299	0.0004	0.0037
12.1194	0.2160	0.0407	0.2186	0.0362	-0.0026	0.0045
13.9345	0.2559	0.0477	0.2577	0.0433	-0.0017	0.0044
16.0216	0.2944	0.0545	0.2928	0.0508	0.0016	0.0037
18.4212	0.3305	0.0609	0.3363	0.0548	-0.0058	0.0061

21.1803	0.3634	0.0667	0.366	0.0613	-0.0026	0.0054

Chart S6. Plot of Inversion Recovery Data at 89 °C.



CIFIT Guesses and Fit Parameters
Initial values of parameters:
1/T1's
No. 0= 0.7500 No. 1= 0.7500
M(inf)'s
No. 2= 0.3900 No. 3= 0.0620
M(0)-M(inf)'s
No. 4= -0.7700 No. 5= -0.0630
and M(0)'s for reference
No. 4= -0.3800 No. 5= -0.0010
Rates
No. 6= 0.9000

Final Values of Fitted Parameters and Uncertainties:

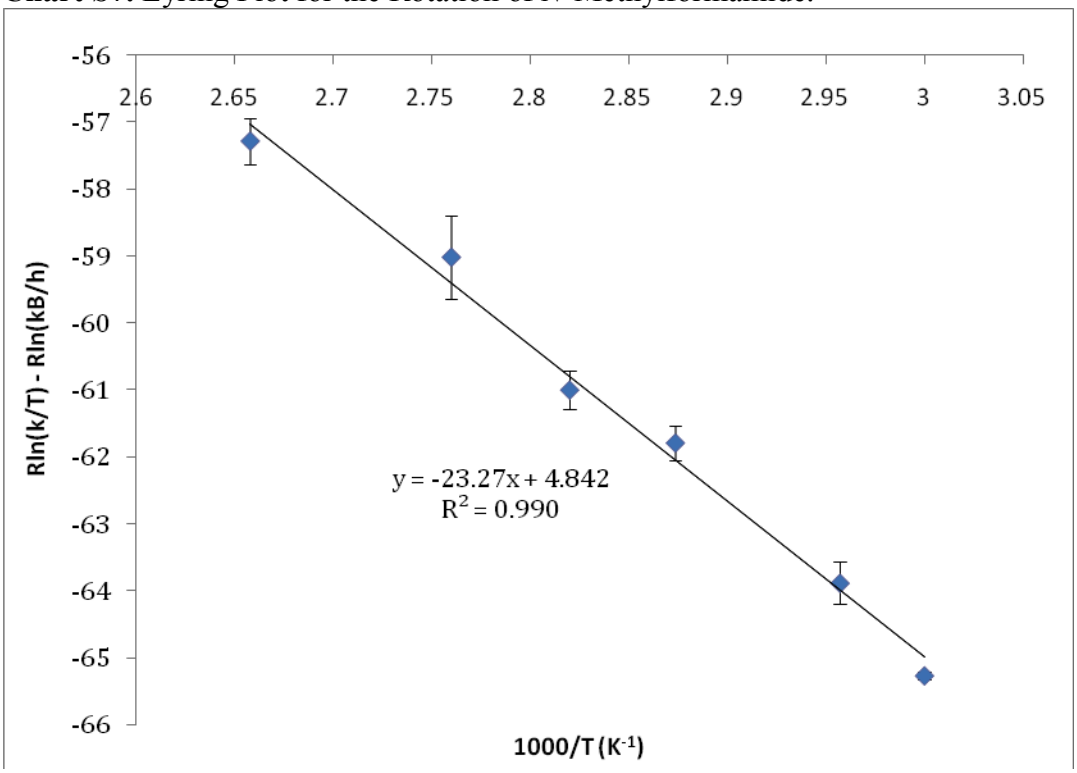
#	0 =	-1.936346 +/-	0.379341
#	1 =	11.595547 +/-	2.301683
#	2 =	0.479191 +/-	0.013684
#	3 =	0.087065 +/-	0.005014
#	4 =	-0.808778 +/-	0.013514
#	5 =	-0.027194 +/-	0.020242
#	6 =	2.460430 +/-	0.456530

IV. Eyring Analysis

Table S7. Data for Eyring Analysis.

T (°C)	T (K)	k (s^{-1})	1000/T (K^{-1})	Rln(k/T) - Rln(k_B/h) (cal/molK)	$\sigma(\Delta H^{\ddagger})$ (kcal/mol)	$\sigma(\Delta S^{\ddagger})$ (eu)
60.33	333.5	$4.0(12) \times 10^{-2}$	3.00	-65.25(77)	0.25	0.96
65.16	338.3	$8.1(14) \times 10^{-2}$	2.96	-63.87(87)	1.42	4.08
74.99	348.1	$2.3(3) \times 10^{-1}$	2.87	-61.78(78)	1.12	3.23
81.61	354.8	$3.6(6) \times 10^{-1}$	2.82	-60.99(90)	1.30	3.73
89.32	362.5	$9.9(36) \times 10^{-1}$	2.76	-59.01(87)	2.99	8.50
103.23	376.4	$2.4(5) \times 10^{0}$	2.66	-57.28(94)	1.52	4.35
					$\langle\sigma(\Delta H^{\ddagger})\rangle$	$\langle\sigma(\Delta S^{\ddagger})\rangle$
					1.44	4.14

Chart S7. Eyring Plot for the Rotation of *N*-Methylformamide.



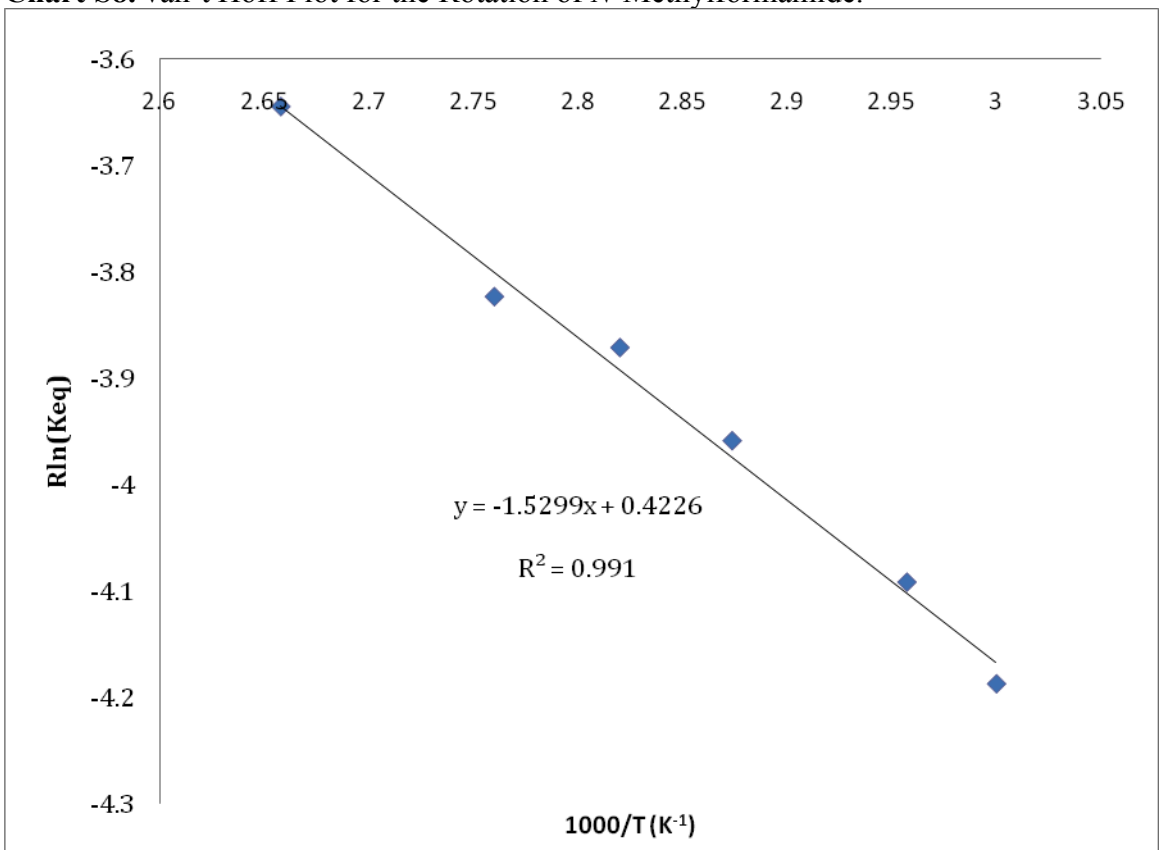
$\Delta H^{\ddagger}$ = 23.2(7) kcal/mol; $\Delta S^{\ddagger}$ = 4.8(42) eu; R^2 = 0.990. R = 1.99 cal/mol K. eu ≡ cal/mol K.

V. van't Hoff Analysis

Table S8. Data for van't Hoff Analysis.

T (°C)	T (K)	1000/T (K^{-1})	Final M(**E**)	Final M(**Z**)	K_{eq}	Rln(K_{eq}) (cal/mol K)
60.33	333.5	3.00	0.0996	0.817	1.22×10^{-1}	-4.19
65.16	338.3	2.96	0.0667	0.521	1.28×10^{-1}	-4.09
74.99	348.1	2.87	0.0788	0.576	1.37×10^{-1}	-3.96
81.61	354.8	2.82	0.0877	0.613	1.43×10^{-1}	-3.87
89.32	362.5	2.76	0.0609	0.416	1.46×10^{-1}	-3.82
103.23	376.4	2.66	0.0929	0.580	1.60×10^{-1}	-3.64

Chart S8. van't Hoff Plot for the Rotation of *N*-Methylformamide.



ΔH = 1.53(7) kcal/mol; ΔS = 0.4(2) eu; R^2 = 0.991. Error bars represent standard error in linear fit as reported by Microsoft Excel's linest function.

V. Simplified McConnell-Bloch Equations

$$\frac{d}{dt}M_z^A = \frac{M_0^A}{T_{1A}} - \frac{M_z^A}{\tau_{1A}} \qquad \frac{d}{dt}M_z^B = \frac{M_0^B}{T_{1B}} - \frac{M_z^B}{\tau_{1B}}$$

where

$$\frac{1}{\tau_{1A}} = \frac{1}{\tau_A} - \frac{1}{T_{1A}} \qquad \frac{1}{\tau_{1B}} = \frac{1}{\tau_B} - \frac{1}{T_{1B}}$$

and $\tau_{A,B}$ are the lifetimes of magnetization in sites A, B.