

Supporting Information: Absorption spectra and photolysis of methyl peroxide in liquid and frozen water

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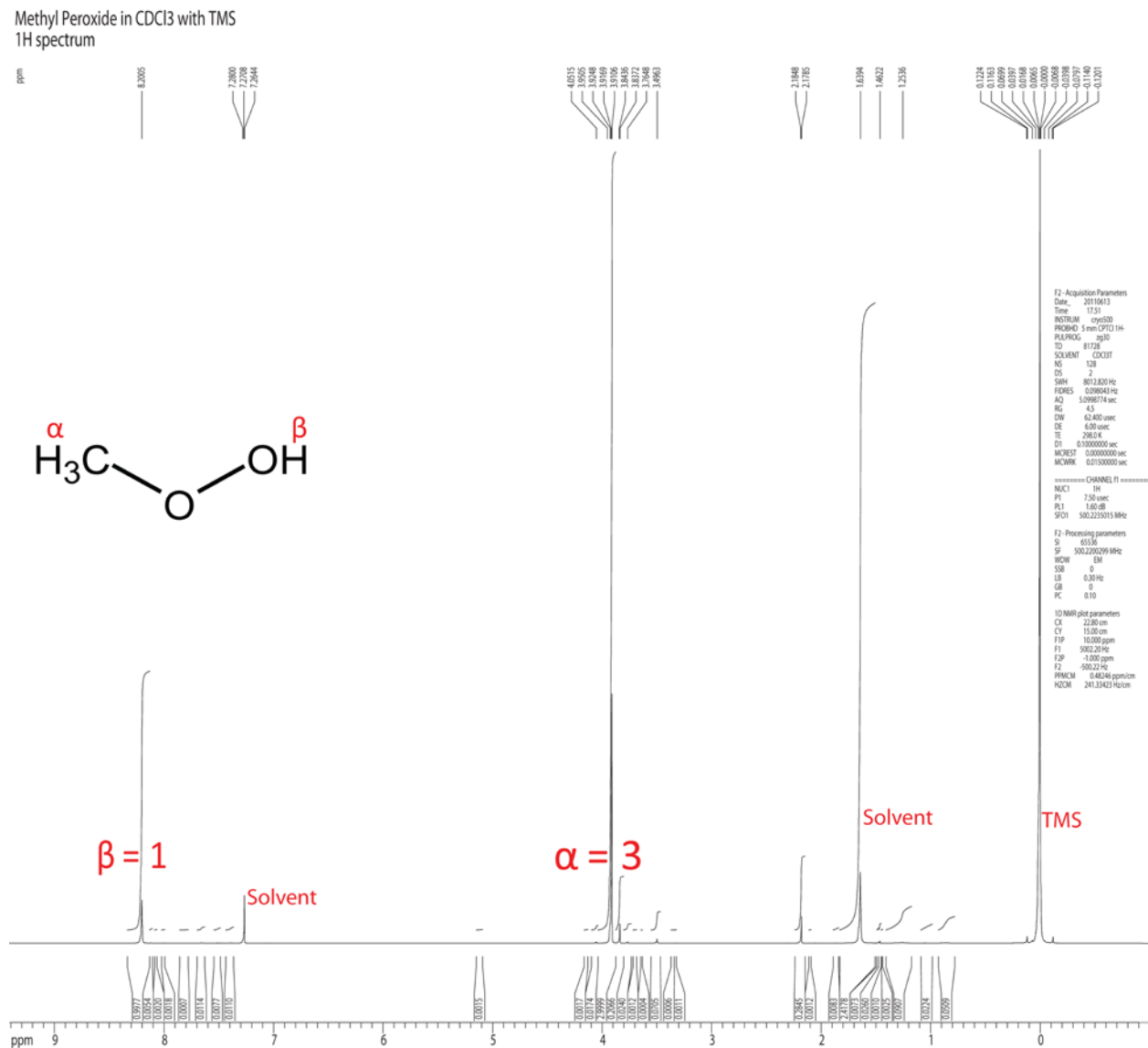


Fig. S1 ¹H-NMR results showing the presence of methyl peroxide in a solution of deuterated chloroform. NMR-peaks due to the presence of the chloroform product are labeled “Solvent”. Tetramethylsilane (TMS) was used as an internal standard to calibrate the NMR spectrum. The two strongest product peaks have areas of 0.9977 and 2.999 representing the hydrogens in the methyl group and the hydrogen in the peroxide group, respectively.

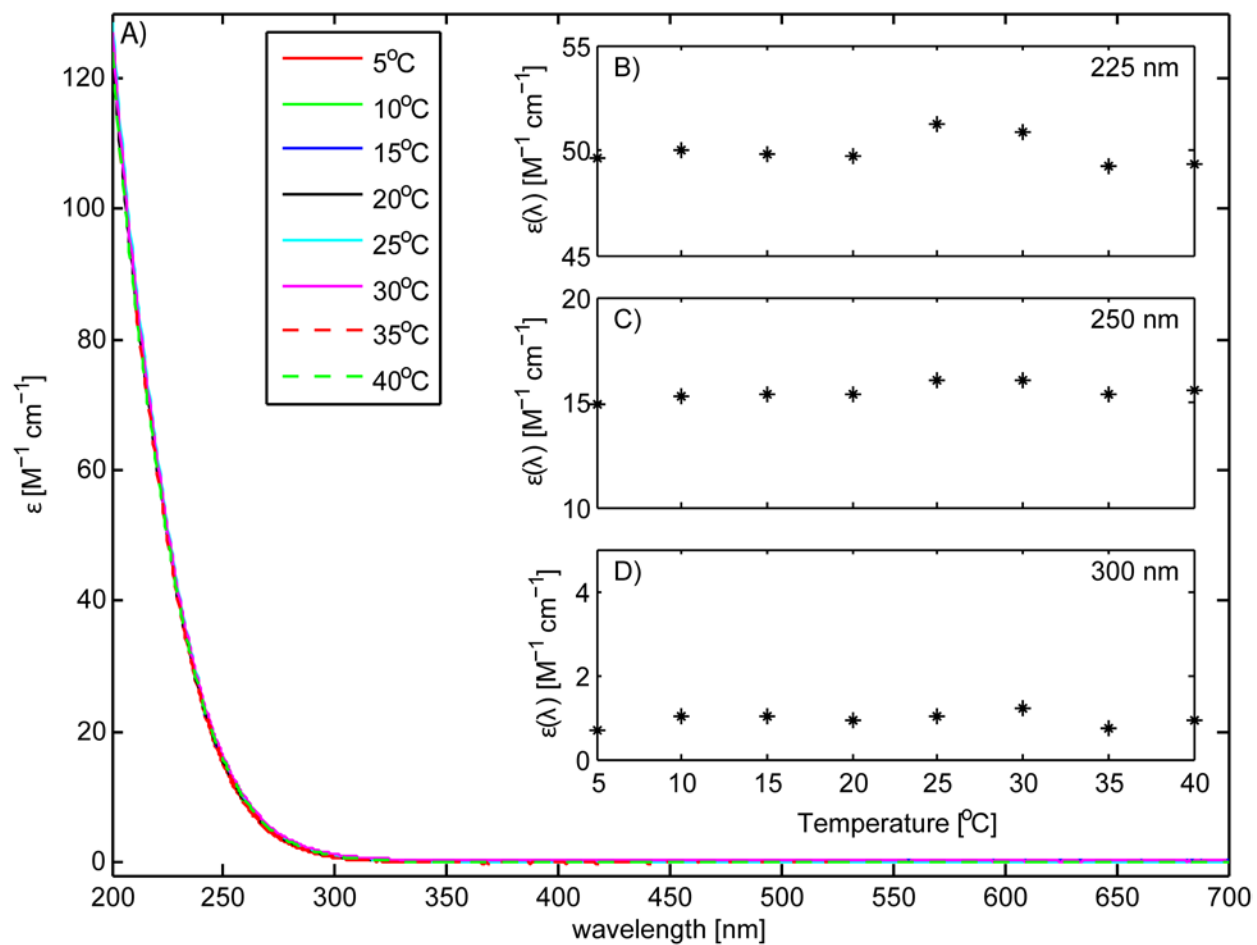


Fig. S2 A) Extinction coefficients of methyl peroxide at temperatures between 5 and 40°C. Variation in the B) 250 nm, C) 225 nm, and D) 300 nm extinction coefficients as a function of temperature. The lack of a trend indicates that variations are due solely to experimental uncertainties and are not the result of an absorption temperature dependence.

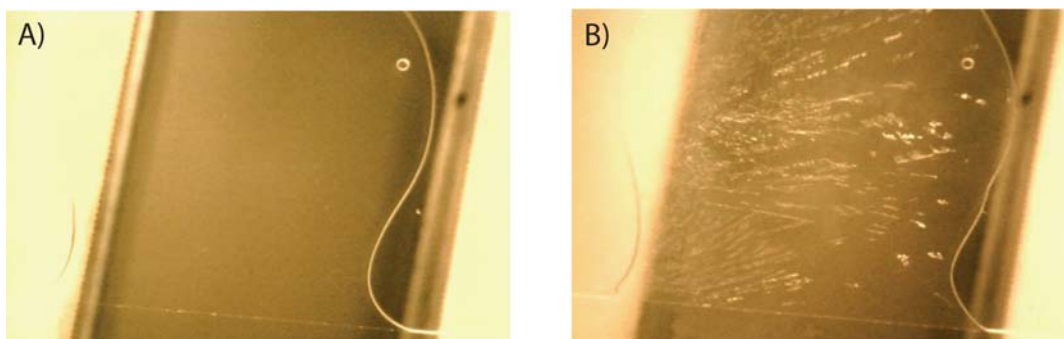


Fig. S3 A) liquid aqueous CH₃OOH solution. B) Frozen CH₃OOH solution.

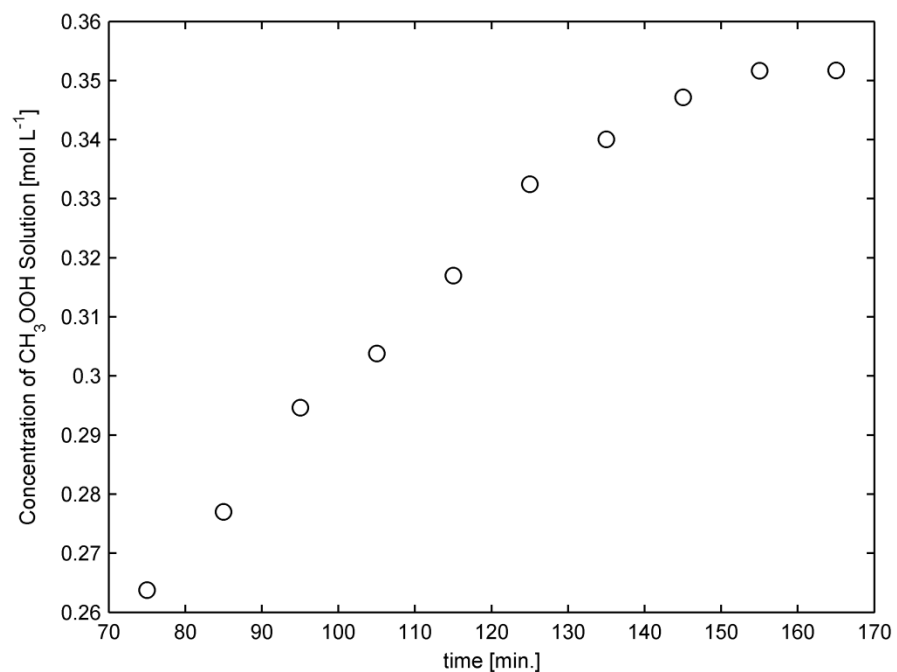


Fig. S4 Predicted concentration of a dilute aqueous CH₃OOH solution as a function of reaction time using the iodometric peroxide test. This plot demonstrates that it is crucial to ensure that the peroxide/KI reaction has reached equilibrium. For certain peroxides, such as methyl peroxide, one must observe the reacting solution significantly longer than the one hour timeframe suggested in Banerjee and Budke.¹

Table 1 Extinction coefficients of liquid and frozen aqueous CH₃OOH in units of [M⁻¹ cm⁻¹] as a function of wavelength measured using dilute solutions [0 to 0.16 M].

wavelength [nm]	ϵ [M ⁻¹ cm ⁻¹]	wavelength [nm]	ϵ [M ⁻¹ cm ⁻¹]	wavelength [nm]	ϵ [M ⁻¹ cm ⁻¹]	wavelength [nm]	ϵ [M ⁻¹ cm ⁻¹]	wavelength [nm]	ϵ [M ⁻¹ cm ⁻¹]
200	126.44	235.5	31.89	271	4.99	306.5	0.62	342	0.09
200.5	125.29	236	31.18	271.5	4.84	307	0.61	342.5	0.10
201	123.06	236.5	30.48	272	4.70	307.5	0.58	343	0.06
201.5	120.89	237	29.78	272.5	4.57	308	0.55	343.5	0.03
202	118.78	237.5	29.10	273	4.47	308.5	0.54	344	0.06
202.5	116.72	238	28.44	273.5	4.35	309	0.52	344.5	0.09
203	114.65	238.5	27.77	274	4.22	309.5	0.48	345	0.11
203.5	112.60	239	27.12	274.5	4.09	310	0.47	345.5	0.09
204	110.62	239.5	26.49	275	3.98	310.5	0.49	346	0.10
204.5	108.72	240	25.85	275.5	3.87	311	0.49	346.5	0.14
205	106.88	240.5	25.26	276	3.76	311.5	0.46	347	0.15
205.5	105.06	241	24.67	276.5	3.63	312	0.43	347.5	0.12
206	103.24	241.5	24.08	277	3.52	312.5	0.43	348	0.07
206.5	101.48	242	23.49	277.5	3.44	313	0.42	348.5	0.04
207	99.79	242.5	22.92	278	3.35	313.5	0.38	349	0.04
207.5	98.11	243	22.38	278.5	3.25	314	0.34	349.5	0.04
208	96.40	243.5	21.84	279	3.17	314.5	0.32	350	0.05
208.5	94.78	244	21.31	279.5	3.08	315	0.35	350.5	0.06
209	93.25	244.5	20.77	280	3.00	315.5	0.36	351	0.09
209.5	91.70	245	20.25	280.5	2.91	316	0.33	351.5	0.10
210	90.11	245.5	19.76	281	2.81	316.5	0.31	352	0.07
210.5	88.51	246	19.29	281.5	2.72	317	0.32	352.5	0.04
211	87.03	246.5	18.82	282	2.64	317.5	0.32	353	0.06
211.5	85.61	247	18.36	282.5	2.56	318	0.31	353.5	0.08
212	84.18	247.5	17.89	283	2.47	318.5	0.28	354	0.00
212.5	82.75	248	17.45	283.5	2.39	319	0.27	354.5	0.00
213	81.33	248.5	17.01	284	2.33	319.5	0.28	355	0.00
213.5	79.90	249	16.59	284.5	2.30	320	0.28	355.5	0.00
214	78.54	249.5	16.19	285	2.23	320.5	0.25	356	0.00
214.5	77.18	250	15.79	285.5	2.17	321	0.22	356.5	0.00
215	75.77	250.5	15.41	286	2.12	321.5	0.23	357	0.00
215.5	74.38	251	15.04	286.5	2.05	322	0.26	357.5	0.00
216	73.02	251.5	14.66	287	1.99	322.5	0.26	358	0.00
216.5	71.69	252	14.30	287.5	1.92	323	0.26	358.5	0.00
217	70.38	252.5	13.94	288	1.85	323.5	0.24	359	0.00
217.5	69.05	253	13.56	288.5	1.80	324	0.23	359.5	0.00
218	67.75	253.5	13.19	289	1.76	324.5	0.23	360	0.00
218.5	66.50	254	12.83	289.5	1.71	325	0.21	360.5	0.00
219	65.26	254.5	12.48	290	1.65	325.5	0.18	361	0.00
219.5	64.02	255	12.15	290.5	1.61	326	0.17	361.5	0.00
220	62.76	255.5	11.85	291	1.59	326.5	0.20	362	0.00
220.5	61.49	256	11.55	291.5	1.55	327	0.21	362.5	0.00
221	60.24	256.5	11.25	292	1.47	327.5	0.17	363	0.00
221.5	59.02	257	10.97	292.5	1.40	328	0.17	363.5	0.00
222	57.83	257.5	10.71	293	1.35	328.5	0.17	364	0.00
222.5	56.63	258	10.43	293.5	1.32	329	0.17	364.5	0.00
223	55.43	258.5	10.12	294	1.28	329.5	0.16	365	0.00
223.5	54.30	259	9.82	294.5	1.23	330	0.14	365.5	0.00
224	53.18	259.5	9.55	295	1.21	330.5	0.14	366	0.00
224.5	52.06	260	9.30	295.5	1.19	331	0.17	366.5	0.00
225	50.95	260.5	9.03	296	1.17	331.5	0.16	367	0.00
225.5	49.89	261	8.78	296.5	1.12	332	0.12	367.5	0.00
226	48.87	261.5	8.56	297	1.07	332.5	0.11	368	0.00
226.5	47.84	262	8.35	297.5	1.04	333	0.12	368.5	0.00
227	46.81	262.5	8.11	298	1.02	333.5	0.15	369	0.00
227.5	45.78	263	7.86	298.5	0.97	334	0.14	369.5	0.00
228	44.77	263.5	7.66	299	0.91	334.5	0.11	370	0.00
228.5	43.79	264	7.47	299.5	0.86	335	0.11	370.5	0.00
229	42.82	264.5	7.28	300	0.86	335.5	0.12	371	0.00
229.5	41.84	265	7.06	300.5	0.87	336	0.11	371.5	0.00
230	40.90	265.5	6.84	301	0.84	336.5	0.10	372	0.00
230.5	39.96	266	6.67	301.5	0.82	337	0.10	372.5	0.00
231	39.06	266.5	6.49	302	0.82	337.5	0.12	373	0.00
231.5	38.20	267	6.30	302.5	0.81	338	0.14	373.5	0.00
232	37.35	267.5	6.10	303	0.76	338.5	0.13	374	0.00
232.5	36.53	268	5.92	303.5	0.69	339	0.11	374.5	0.00
233	35.73	268.5	5.76	304	0.66	339.5	0.14	375	0.00
233.5	34.92	269	5.60	304.5	0.65	340	0.15	375.5	0.00
234	34.12	269.5	5.44	305	0.63	340.5	0.13	376	0.00
234.5	33.37	270	5.26	305.5	0.58	341	0.08	376.5	0.00
235	32.63	270.5	5.12	306	0.59	341.5	0.07	377	0.00

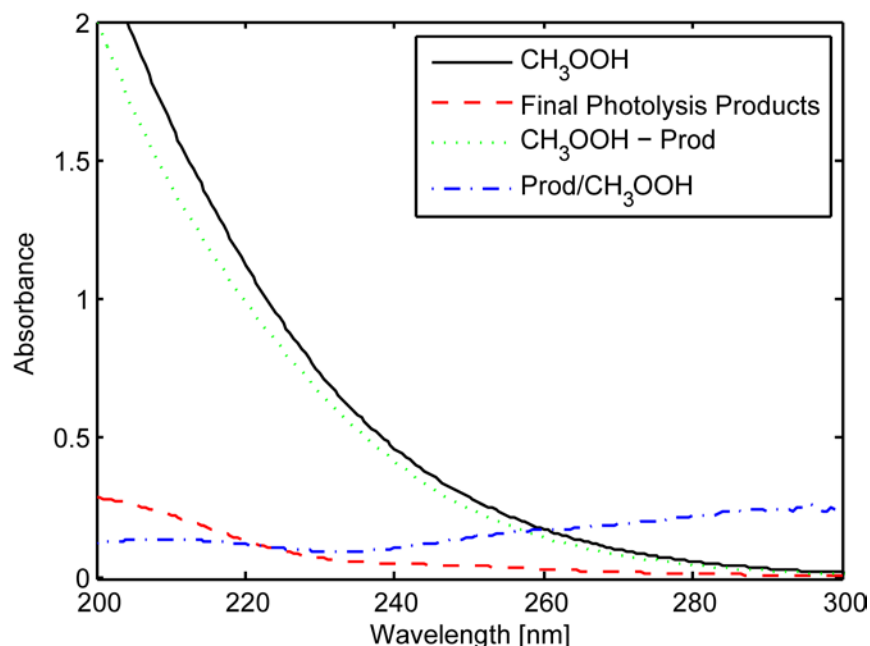


Fig. S5 Liquid aqueous CH_3OOH photolysis products absorption spectrum relative to the initial CH_3OOH spectrum. At wavelengths greater than 230 nm, the equilibrium product signal is no greater than 10% of the initial methyl peroxide signal supporting the approximation that the absorption spectra of the photolyzed CH_3OOH solution is proportional to the concentration of CH_3OOH at the limit of short photolysis times.

Vertical excitation calculations

Table 2 shows the vertical excitation energy of the bare and solvated methyl peroxide in the water cluster as calculated with OM2 and with ADC(2).

Table 2 Vertical excitation energy for the bare and solvated methyl peroxide as calculated by ADC(2) and OM2.

	Bare CH_3OOH	Solvated CH_3OOH	Solvatochromic shift
ADC(2) vertical excitation energy (in eV)	6.18	6.69	0.51
OM2 vertical excitation energy (in eV)	3.43	3.84	0.41

OM2 is a semiempirical method that is parameterized for certain systems leading us to believe that this is the cause of the differences in the excitation energy. Qualitatively, the excited state described by OM2 is similar to the one described by ADC(2). The solvatochromic shifts predicted by OM2 and ADC(2) are similar. The full potential energy surface as a function of O-O distance calculated with both methods is presented in Figure S6.

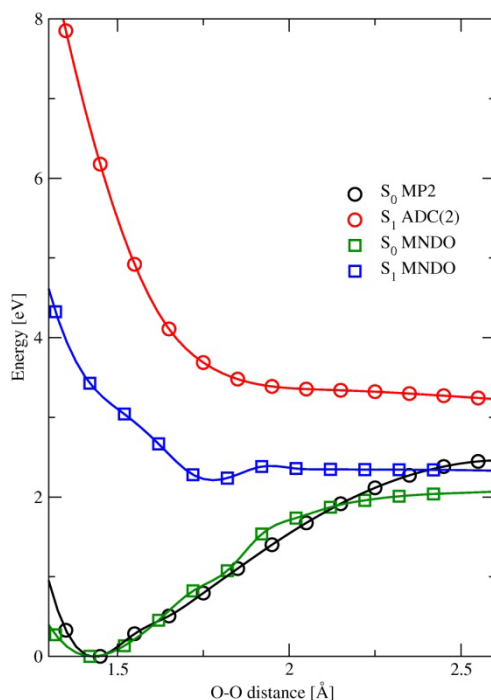


Fig S6: Potential energy surface as a function of O-O distance as calculated by OM2 and ADC(2)

Both methods predict that the first excited state is dissociative along the O-O distance. Kamboures et. al² find the same result with the CIS method. Qualitatively, the OM2 method describes the correct photophysical behaviour when considering the solvatochromic shift and the behaviour of the excited state along the O-O distance. Therefore, we are confident that the OM2 method can be used to predict the excitation spectrum of the bare methyl peroxide compared to the solvated methyl peroxide.

References

1. D. K. Banerjee and C. C. Budke, *Analytical Chemistry*, 1964, **36**, 792-796.
2. M. A. Kamboures, S. A. Nizkorodov and R. B. Gerber, *Proceedings of the National Academy of Sciences*, 2010, **107**, 6600-6604.