Supporting Information for Ab initio Molecular Dynamics Simulation of Vibrational Energy Redistribution of Selective Excitation of C−H Stretching Vibrations for Solid Nitromethane

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Author Contributions

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Strong coupling and weak coupling

In this work, the strong coupling and weak coupling between the normal modes were defined by the SED spectra. For example, Figure S1, S2 and S3 exhibit the SED spectra for the 14 intramolecular modes obtained from STFT of their normal-mode momentum ranging from 11 to 12 ps after excitation of mode 74, 80, and 84, respectively. According to the SED in these spectra, the mode itself is always in the order of 0.1 a.u.. To generally distinguish the coupling modes, the concomitant coupling modes which could be more than 1.0×10^{-3} a.u. are defined as strong coupling (mainly under the second excitation), and those always in the order of 1.0×10^{-4} a.u. are defined as weak coupling.

Table S1. Vibrational frequencies (in cm^{-1}) of internal and external modes of solid nitromethane. All quantities are calculated at the respective theoretical equilibrium volume using PBE-D3 functional. Here A(R), B1(R+IR), B2(R+IR) and B3(R+IR) are irreducible representations of space group $P2_12_12_1$, and A1(R+IR), A2(R+IR), B1(R+IR) and B2(R+IR) are irreducible representation of point group C_{2v}. Note that anharmonic frequencies are obtained from Fourier transformation of kinetic energy of normal modes.

Crystalline nitromethane ($P2_12_12_1$)					Molecular nitromethane (C_{2v}) [a]		
No.	Harmonic frequency	Anharmonic frequency	Irreducible representation	Assignment	Mode	Irreducible representation	Assignment (notion)
4	52.2	56	B2	CH_3 rotation	M15	A2	CH_3 torsion $\tau(NO_2)$
5	54.3	61	B1				
6	54.8	56	A				
7	61.5	61	B3				
8	71.9	74	A	--	--	--	--
9	73.5	74	B2	--	--	--	--
10	76.1	74	B1	--	--	--	--
11	76.2	74	A	--	--	--	--
12	79.5	76	B1	--	--	--	--
13	88.1	84	A	--	--	--	--
14	93.1	91	B2	--	--	--	--
15	94.1	89	B3	--	--	--	--
16	102.8	102	B3	--	--	--	--
17	108.8	107	B1	--	--	--	--
18	108.9	107	A	--	--	--	--
19	111.6	114	B3	--	--	--	--
20	115.0	114	B2	--	--	--	--
21	117.2	114	B3	--	--	--	--
22	118.4	117	B1	--	--	--	--
23	124.3	117	B2	--	--	--	--
24	129.3	130	A	--	--	--	--

Continued.

Crystalline nitromethane ($P2_12_12_1$)					Molecular nitromethane (C_{2v})		
No.	Harmonic frequency	Anharmonic frequency	Irreducible representation	Assignment	Mode	Irreducible representation	Assignment
25	140.7	135	A	--	--	--	--
26	145.5	142	B3	--	--	--	--
27	150.5	147	B2	--	--	--	--
28	152.4	150	B1	--	--	--	--
29	477.8	478	B1	NO_2 rocking	M14	B1	NO_2 rocking $\rho(NO_2)$
30	478.3	478	B3				
31	478.4	478	A				
32	480.3	478	B2				
33	588.5	590	A	NCH wagging + NO_2 out of plane wagging	M13	B2	NO_2 rocking $\rho(NO_2)$
34	589.3	590	B3				
35	593.7	595	B2				
36	595.2	597	B1				
37	646.6	646	A	CN stretching + NO_2 scissor	M12	A1	NO_2 symmetric bending $\delta_s(NO_2)$
38	650.0	648	B2				
39	650.5	648	B3				
40	652.9	653	B1				
41	909.5	910	B3	CN stretching + NO_2 bending	M11	A1	CN stretching $\upsilon(CN)$
42	909.6	910	B1				
43	910.1	910	A				
44	910.6	910	B2				
45	1078.0	1080	B1	CH_3 twisting + NO_2 asymmetrical stretching	M10	B1	CH_3 rocking $\rho(CH_3)$
46	1079.2	1080	B2				
47	1080.2	1080	A				
48	1081.6	1086	B3				

Continued.

Crystalline nitromethane ($P2_12_12_1$)					Molecular nitromethane (C_{2v})		
No.	Harmonic frequency	Anharmonic frequency	Irreducible representation	Assignment	Mode	Irreducible representation	Assignment
49	1085.4	1086	A	NCH deformation	M9	B2	CH_3 rocking $\rho(CH_3)$
50	1086.6	1088	B3				
51	1087.6	1088	B1				
52	1092.7	1093	B2				
53	1338.3	1340	B3	CH_3 wagging + NO_2 symmetric stretching + CN stretching	M8	A1	CH_3 symmetric bending $\delta_s(CH_3)$
54	1340.9	1343	A				
55	1341.1	1343	B2				
56	1341.7	1343	B1				
57	1381.3	1383	A	CH_3 deformation + NO_2 symmetric stretching	M7	A1	NO_2 symmetric stretching $\upsilon_s(NO_2)$
58	1384.9	1388	B3				
59	1394.5	1396	B2				
60	1391.6	1394	B1				
61	1391.5	1394	A	CH_3 deformation + NO_2 symmetric stretching	M6	B1	CH_3 asymmetrical bending $\delta_{as}(CH_3)$
62	1395.3	1399	B3				
63	1402.1	1409	B1				
64	1409.9	1414	B2				
65	1415.8	1419	A	CH_3 deformation + NO_2 asymmetrical stretching	M5	B2	CH_3 asymmetrical bending $\delta_{as}(CH_3)$
66	1416.1	1416	B2				
67	1425.5	1429	B3				
68	1435.0	1437	B1				
69	1532.6	1533	A	CH_3 wagging + NO_2 asymmetrical stretching	M4	B1	NO_2 asymmetrical stretching $\upsilon_{as}(NO_2)$
70	1553.8	1554	B1				
71	1559.3	1556	B3				
72	1561.2	1564	B2				

Continued.

Crystalline nitromethane ($P2_12_12_1$)					Molecular nitromethane (C_{2v})		
No.	Harmonic frequency	Anharmonic frequency	Irreducible representation	Assignment	Mode	Irreducible representation	Assignment
73	3003.6	3019	B3	CH_3 symmetric stretching	M3	A1	CH_3 symmetric stretching $\upsilon_s(CH_3)$
74	3004.2	3021	A				
75	3004.6	3021	B1				
76	3005.9	3021	B2				
77	3103.0	3118	B3	CH_3 asymmetrical stretching	M2	B2	CH_3 asymmetrical stretching $\upsilon_{as}(CH_3)$
78	3103.5	3118	A				
79	3103.9	3118	B1				
80	3104.7	3118	B2				
81	3151.9	3166	A	CH_3 asymmetrical stretching	M1	B1	CH_3 asymmetrical stretching $\upsilon_{as}(CH_3)$
82	3152.0	3166	B3				
83	3152.7	3166	B2				
84	3153.6	3169	B1				

[a] Ref. J. Chem. Phys. 108, 7350 (1998).

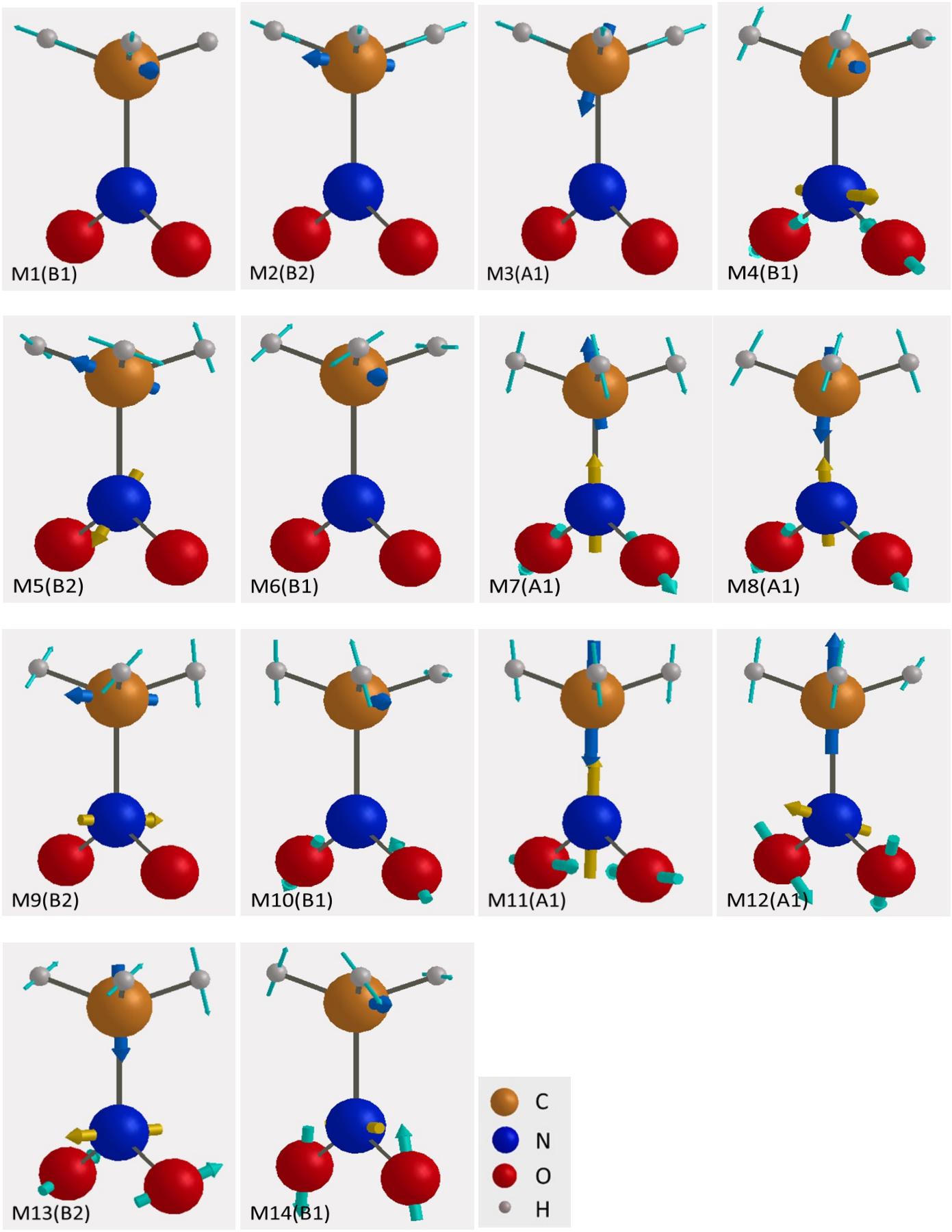

Figure S1. Graphical depictions of the 14 intramolecular vibrations.

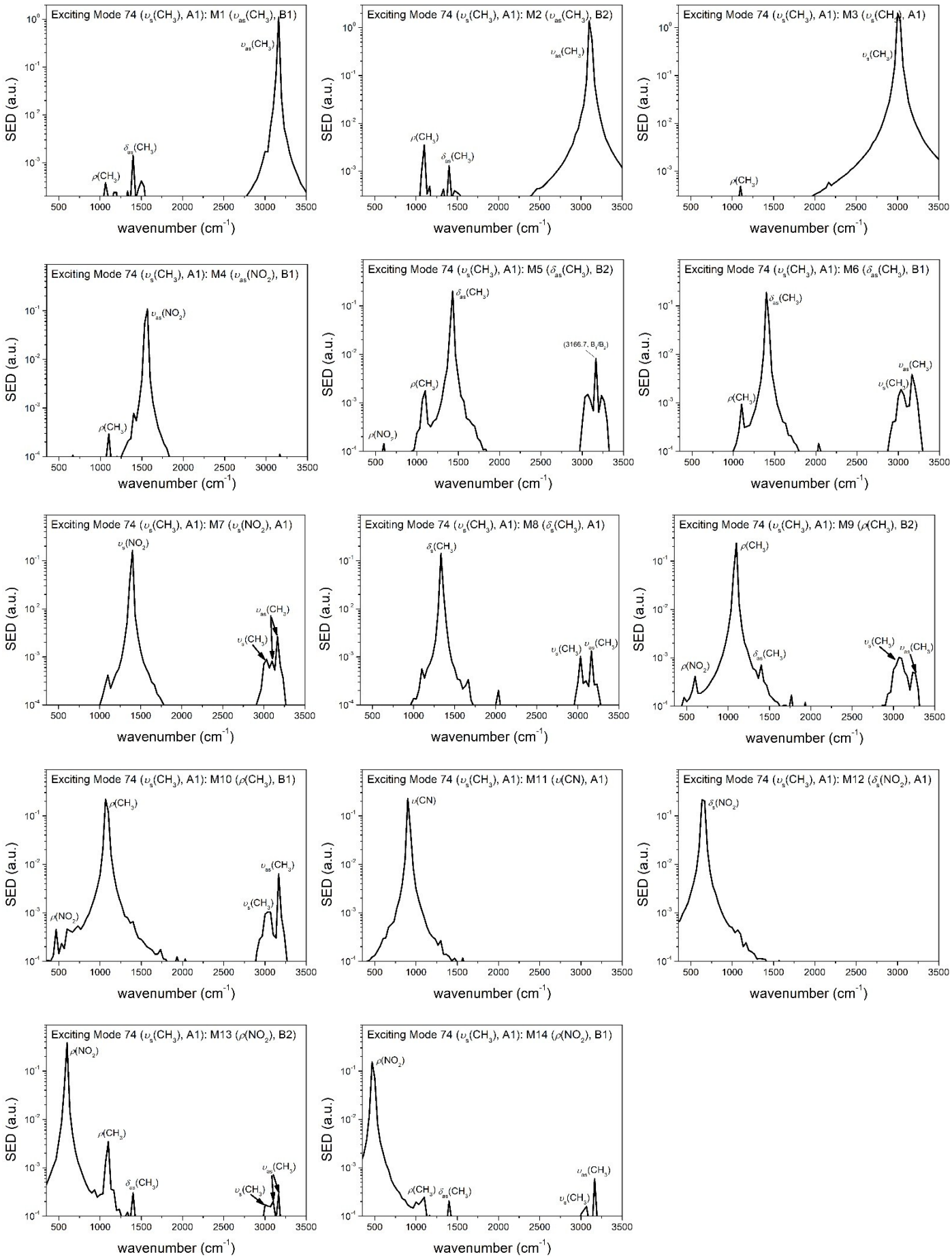

Figure S2. SED spectra between 11 and 12 ps of intramolecular mode after exciting mode 74 (C-H symmetric stretching).

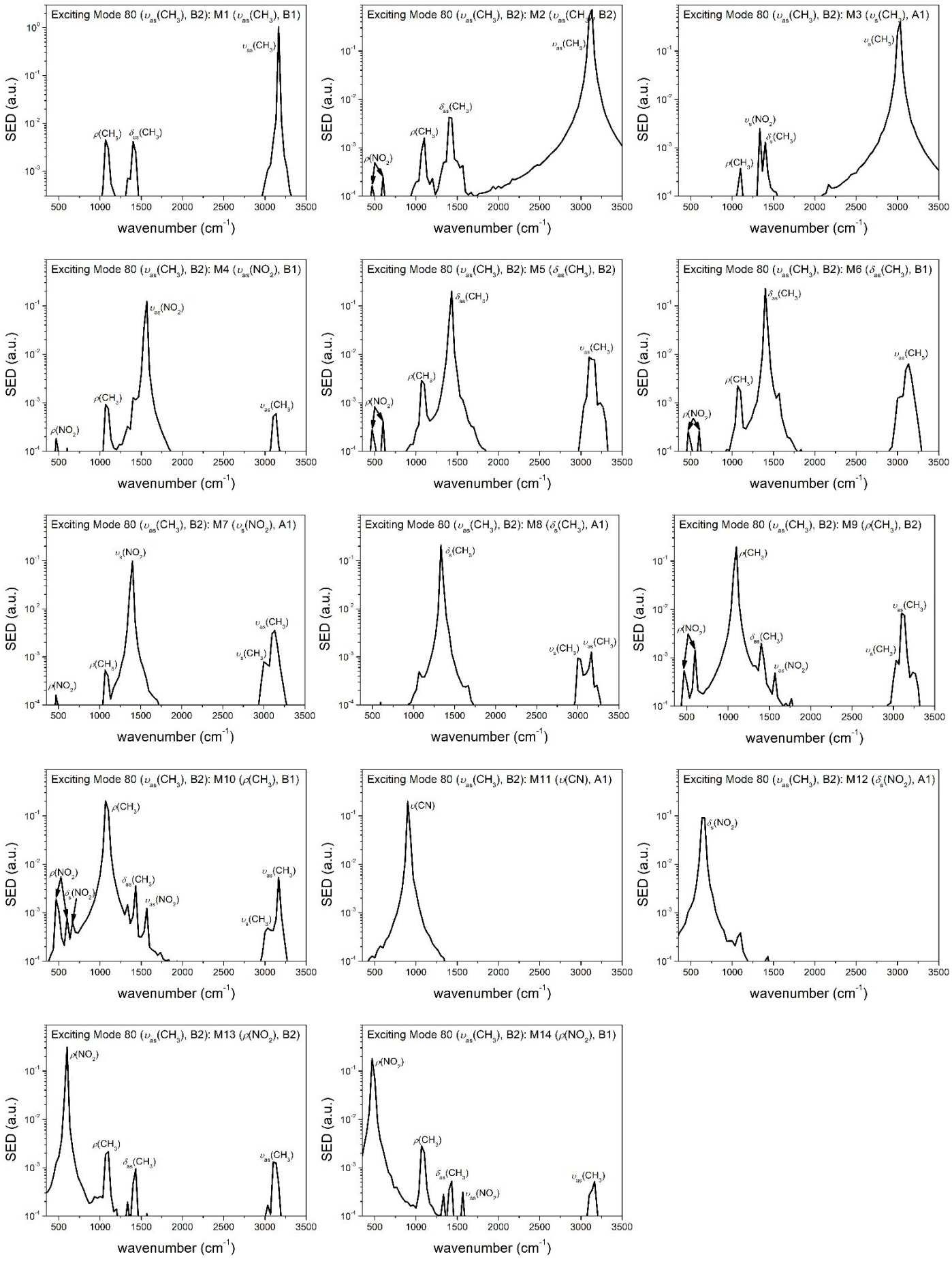

Figure S3. SED spectra between 11 and 12 ps of intramolecular mode after exciting mode 80 (C-H asymmetric stretching).

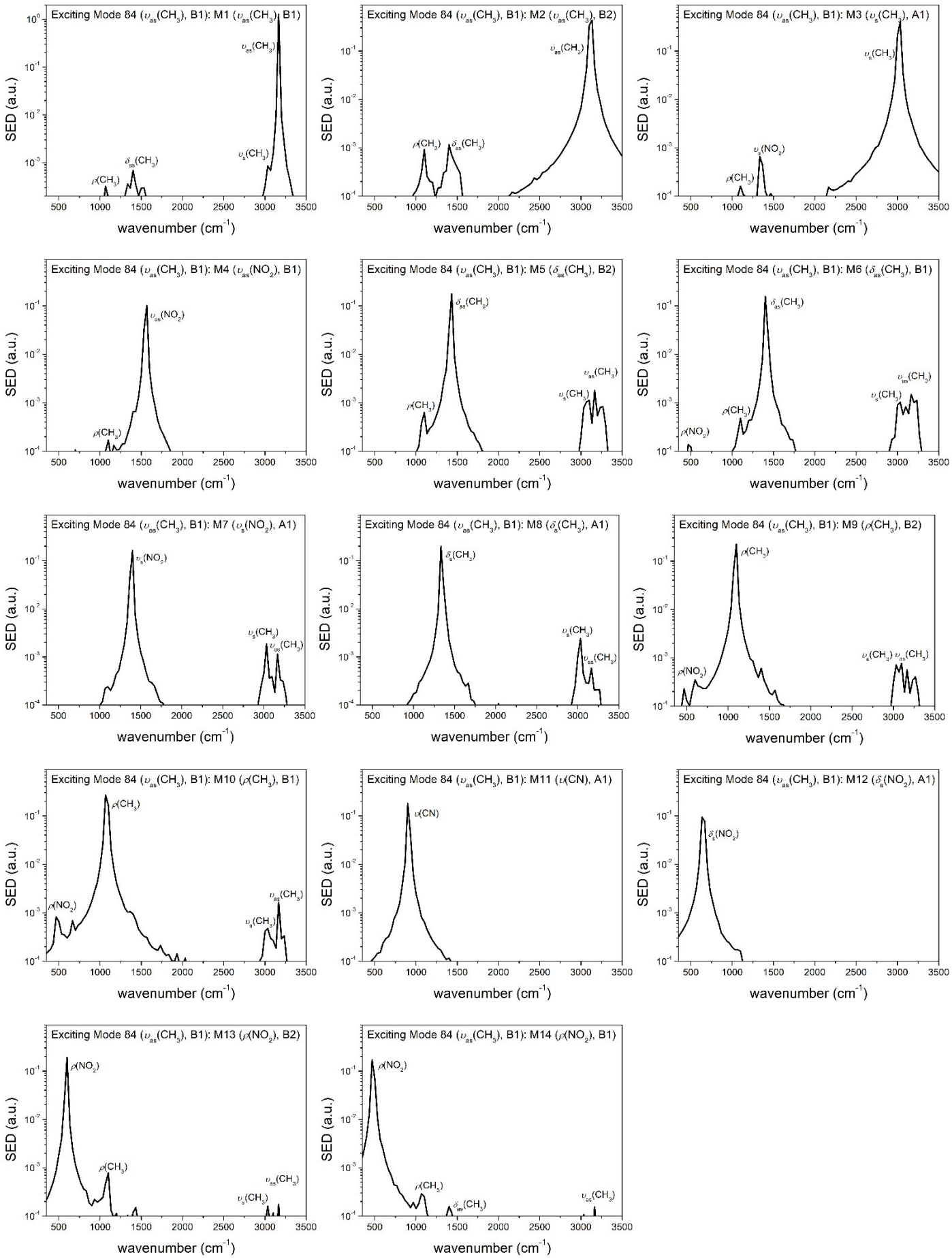

Figure S4. SED spectra between 11 and 12 ps of intramolecular mode after exciting mode 84 (C-H asymmetric stretching).

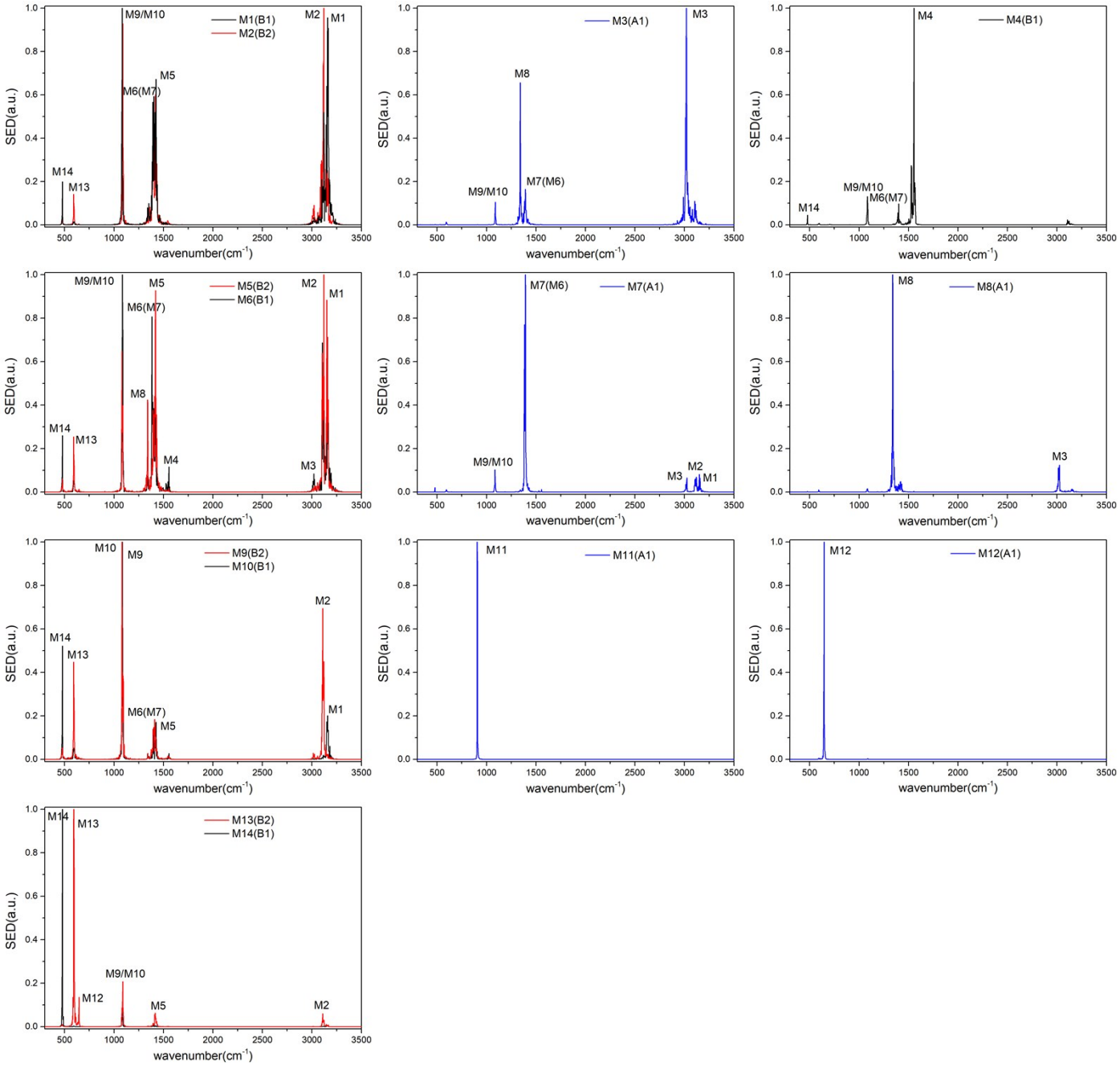

Figure S5. SED spectra in 12 ps of intramolecular mode at 100 K without selective excitation. The lines were colored in black, red and blue according to their symmetries B1, B2 and A1.

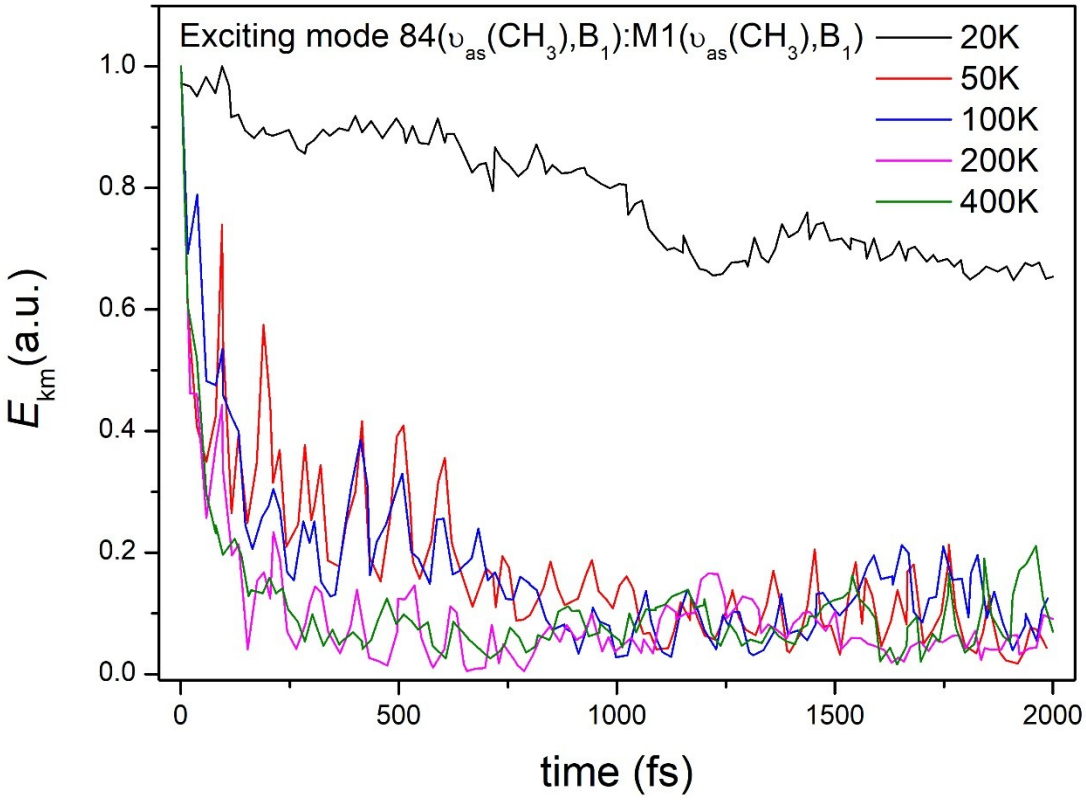

Figure S6. Evolution of kinetic energy for intramolecular mode M1 ($\upsilon_{as}(CH_3)$) after exciting mode 84 (C-H asymmetric stretching).

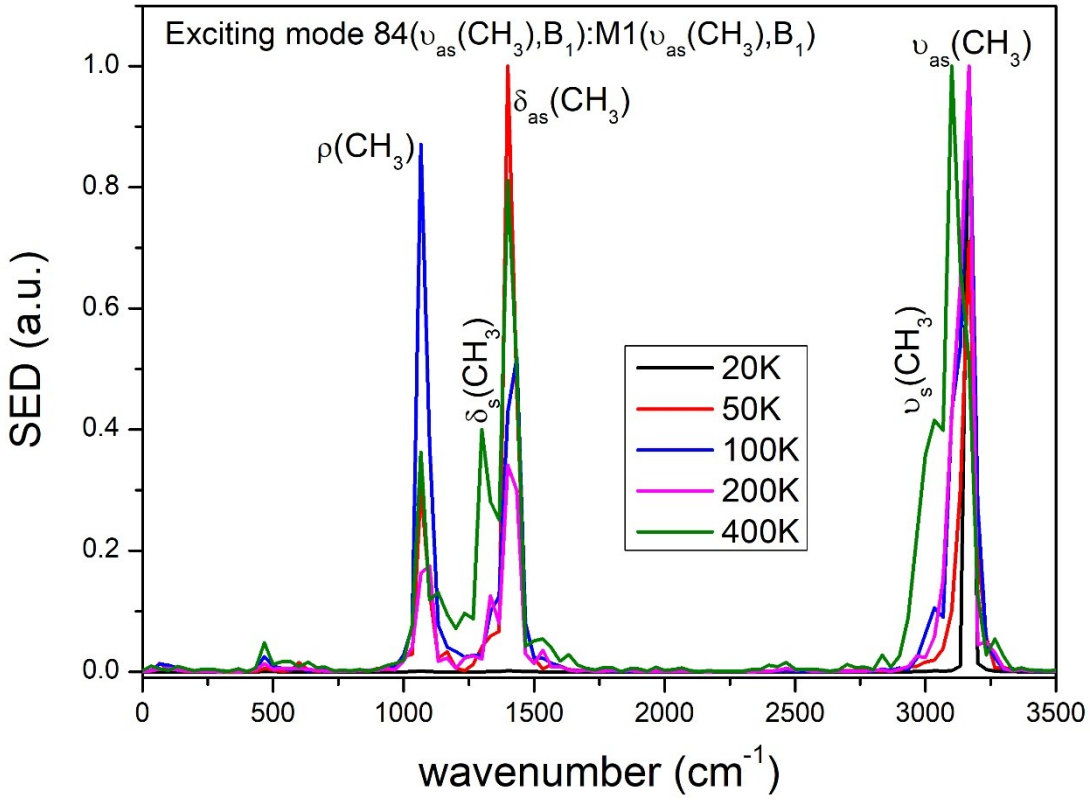

Figure S7. SED spectra of intramolecular mode M1 ($\upsilon_{as}(CH_3)$) for the first 1 ps after exciting mode 84 (C-H asymmetric stretching).