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 $P_{2_12_12_1}$, 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	Anharmonic	Irreducible	Assignment	Mode	Irreducible	Assignment (notion)	
	52.2	56	P2			representation		
- - 5	54.3	61	B1					
5	54.9	56		CH ₃ rotation	M15	A2	CH ₃ torsion $\tau(NO_2)$	
0 7	54.0 61.5	50 61	R3					
	71.0	74	B5					
0	72.5	74	A D2					
9 10	75.5	74	D2 D1					
10	76.2	74						
12	70.2	74	A D1					
12	79.J 00 1	70 84						
13	02.1	84 01	A D2					
14	95.1	91 80	D2 D3					
15	102.8	102	B3					
17	102.0	102	B1					
17	108.0	107						
10	111.6	107	R3					
20	115.0	114	B3					
20	117.0	114	B2 B3					
21	118.4	117	B3					
22	110. 4 12/13	117	B1 B2					
23 24	124.5	117	Δ					
<i>2</i> 4	147.5	130	A					

Contin	ued.						
		Crystalline	e nitromethane (H	$22_{1}2_{1}2_{1})$		Molecular ni	tromethane (C_{2v})
No.	Harmonic frequency	Anharmonic frequency	Irreducible representation	Assignment	Mode	Irreducible representation	Assignment
25	140.7	135	А				
26	145.5	142	B3				
27	150.5	147	B2				
28	152.4	150	B1				
29	477.8	478	B1				
30	478.3	478	B3	NO rocking	M14	D1	NO realize $q(NO)$
31	478.4	478	А	NO ₂ locking	10114	BI	NO_2 locking $p(NO_2)$
32	480.3	478	B2				
33	588.5	590	А				
34	589.3	590	B3	NCH wagging +	M12	DJ	NO realize (NO)
35	593.7	595	B2	NO2 out of plane wagging	IVI I S	D2	NO_2 focking $\rho(NO_2)$
36	595.2	597	B1				
37	646.6	646	А				
38	650.0	648	B2	CN stratahing + NO saissor	M12	A 1	NO ₂ symmetric bending
39	650.5	648	B3	CN stretching + NO_2 scissor	IVI I Z	AI	$\delta_{\rm s}({ m NO}_2)$
40	652.9	653	B1				
41	909.5	910	B3				
42	909.6	910	B1	CN stratahing + NO handing	M11	A 1	CN stratahing w(CNI)
43	910.1	910	А	CN stretching + NO_2 bending	10111	AI	CN stretching $U(CN)$
44	910.6	910	B2				
45	1078.0	1080	B1				
46	1079.2	1080	B2	CH ₃ twisting +	M10	B1	CH_3 rocking $\rho(CH_3)$
47	1080.2	1080	А	NO2 asymmetrical stretching			
48	1081.6	1086	B3				

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Contin	ued.						
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $			Crystalline	e nitromethane (A	$(2_12_12_1)$		Molecular ni	tromethane (C_{2v})
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	No.	Harmonic frequency	Anharmonic frequency	Irreducible representation	Assignment	Mode	Irreducible representation	Assignment
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	49	1085.4	1086	А				
511087.61088B1NCH deformationM9B2CH3 rocking ρ (CH3)521092.71093B2531338.31340B3CH3 wagging + NO2 symmetric stretching + CN stretchingM8A1CH3 symmetric bending δ_{1} (CH3)541340.91343ACH3 wagging + NO2 symmetric stretchingM8A1CH3 symmetric bending δ_{1} (CH3)551341.11343B2CN stretchingM7A1NO2 symmetric stretching υ_{n} (NO2)571381.31383ANO2 symmetric stretchingM7A1NO2 symmetric stretching 	50	1086.6	1088	B3	NCU deformation	MO	D2	CIL realizes (CIL)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	51	1087.6	1088	B1	NCH deformation	1/19	B2	CH ₃ focking ρ (CH ₃)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	52	1092.7	1093	B2				
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	53	1338.3	1340	B3	CIL wagging			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	54	1340.9	1343	А	CH_3 wagging +	MQ	A1	CH_3 symmetric bending $\delta_{s}(CH_3)$
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	55	1341.1	1343	B2	NO_2 symmetric stretching \pm	IVIO		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	56	1341.7	1343	B1	CN stretching			
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	57	1381.3	1383	А				
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	58	1384.9	1388	В3	CH ₃ deformation +	M7	A 1	NO ₂ symmetric stretching
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	59	1394.5	1396	B2	NO ₂ symmetric stretching	IVI /	AI	$v_{\rm s}({ m NO}_2)$
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	60	1391.6	1394	B1				
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	61	1391.5	1394	А				
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	62	1395.3	1399	B3	CH ₃ deformation +	M6	P 1	CH ₃ asymmetrical bending
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	63	1402.1	1409	B1	NO ₂ symmetric stretching	IVIO	DI	$\delta_{\rm as}({ m CH}_3)$
$ \begin{array}{ccccccccccccccccccccccccc$	64	1409.9	1414	B2				
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	65	1415.8	1419	А				
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	66	1416.1	1416	B2	CH ₃ deformation +	M5	BJ	CH ₃ asymmetrical bending
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	67	1425.5	1429	B3	NO ₂ asymmetrical stretching	IVIJ	D2	$\delta_{\rm as}({ m CH}_3)$
691532.61533A701553.81554B1 CH_3 wagging +711559.31556B3 NO_2 asymmetrical stretching721561.21564B2	68	1435.0	1437	B1				
70 1553.8 1554 B1 CH_3 wagging + M4 B1 NO_2 asymmetrical stretching 71 1559.3 1556 B3 NO_2 asymmetrical stretching M4 B1 $v_{as}(NO_2)$ 72 1561.2 1564 B2 $V_{as}(NO_2)$ $V_{as}(NO_2)$	69	1532.6	1533	А				
71 1559.3 1556 B3 NO2 asymmetrical stretching $v_{as}(NO_2)$ 72 1561.2 1564 B2 $v_{as}(NO_2)$	70	1553.8	1554	B1	CH ₃ wagging +	M4	H B1	NO ₂ asymmetrical stretching $v_{as}(NO_2)$
72 1561.2 1564 B2	71	1559.3	1556	B3	NO2 asymmetrical stretching	1114		
	72	1561.2	1564	B2				

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		Crystallir	ne nitromethane (Molecular nitromethane (C_{2v})			
No.	Harmonic frequency	Anharmonic frequency	Irreducible representation	Assignment	Mode	Irreducible representation	Assignment
73	3003.6	3019	B3				
74	3004.2	3021	Α	CII aummatria strataking	M3	A1	CH ₃ symmetric stretching
75	3004.6	3021	B1	CH ₃ symmetric stretching			$\nu_{\rm s}({\rm CH_3})$
76	3005.9	3021	B2				
77	3103.0	3118	В3				
78	3103.5	3118	А	CH ₃ asymmetrical stretching	M2	B2	CH_3 asymmetrical stretching $v_{as}(CH_3)$
79	3103.9	3118	B1				
80	3104.7	3118	B2				
81	3151.9	3166	А				
82	3152.0	3166	B3	CH ₃ asymmetrical stretching	M1	B1	CH ₃ asymmetrical stretching v_{as} (CH ₃)
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 ($\nu_{as}(CH_3)$) after exciting mode 84 (C-H asymmetric stretching).



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