Vibrational mode Tailoring Approach: An Efficient Route to Compute Anharmonic Molecular Vibrations of Large Molecules

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Contents	**Page**

Figure S9. Normal mode analysis of NATA for a. Anti-symmetric NH_2 stretching (Mode **92**) b. Indole N-H stretching (Mode **93**) c. C=O stretching (Mode **78**) d. NH_2 bending (Mode **51**) e. Symmetric-N-H stretching (Mode **90**) f. φ N-H stretching (Mode **91**)	**S29-S34**

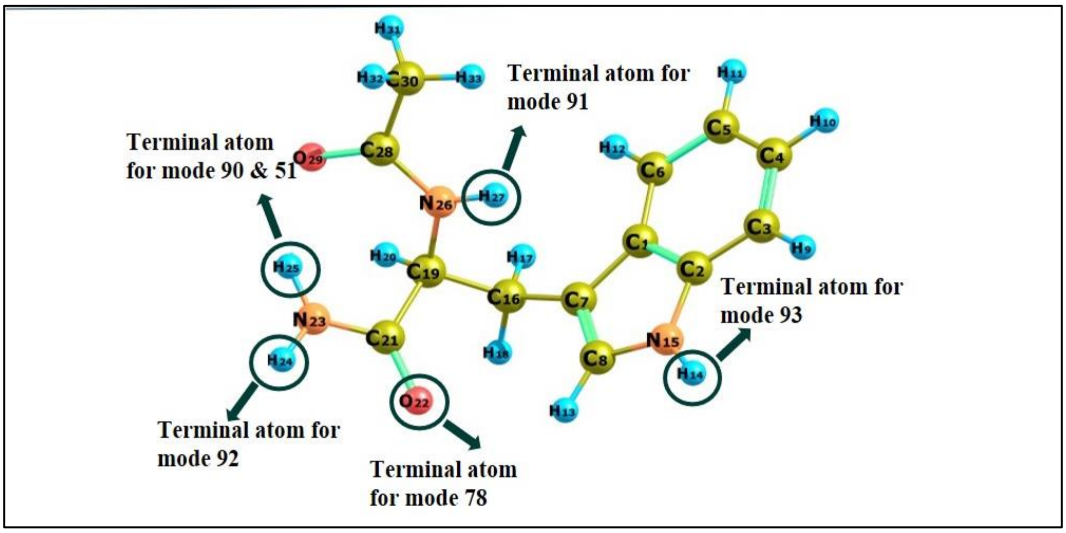

Fig. S1. Pictorial representation of terminal atom encircled for each target mode considered for normal mode analysis: upper panel: butanol and lower panel: NATA.

Calculations of Atomic Mode displacements

We assessed the displacements of target atoms in target normal modes of vibration along with other modes. For a system of *m* atoms with *N* vibrational modes, target mode (*t*) is the mode of interest. To calculate the atomic displacements for a target mode, we mainly focused on the terminal atom and its displacements in different vibrational modes which are coupled with the target mode in different extent. Here, the terminal atom (which is also a target atom) is the one which is connected to other atom only from one side (by single, double bonds, etc.). The component of the atomic displacement vector of atom a for mode i (represented as q_a^i) is calculated, focusing mostly on the terminal atom(s) of the target modes as

$$\mathrm{q}_a^i = \sqrt{\Delta X_a^2 + \Delta Y_a^2 + \Delta Z_a^2} \quad (1)$$

Here, ΔX_a, ΔY_a, and ΔZ_a, are atomic displacements with the unit of length (Å) for i^{th} mode, along *x, y,* and *z* axes from the equilibrium position, respectively. Relative atomic displacements ($\mathrm{q_R}$) of an a^{th} atom for i^{th} mode is then calculated with respect to displacements of same atom for the target mode as,

$$\mathrm{q_R} = q_a^i / q_a^t \quad (2)$$

Since $\mathrm{q_R}$ is ratio of atomic displacements for two different modes, it is technically a unitless quantity. It is aimed to analyse the position of the terminal atom/target atom in various vibrational modes and its comparison with that of target mode.

Table S1a. Calculations of atomic mode displacements for target mode **39** for butanol

Atoms(a)	ΔX	ΔY	ΔZ	$\mathrm{q}_a^i = \sqrt{\Delta X_a^2 + \Delta Y_a^2 + \Delta Z_a^2}$
C1	-0.00002446	0.00004225	0.00000000	0.00
H2	0.00011600	-0.00026649	0.00000000	0.00
H3	0.00000596	0.00002860	-0.00000266	0.00
H4	0.00000595	0.00002859	0.00000266	0.00
C5	0.00005011	-0.00016354	0.00000000	0.00
H6	-0.00011587	0.00040497	0.00046602	0.00
H7	-0.00011585	0.00040501	-0.00046605	0.00
C8	-0.00001257	0.00035821	0.00000000	0.00
H9	0.00068062	0.00024315	-0.00048906	0.00
H10	0.00068063	0.00024313	0.00048904	0.00
C11	-0.00015174	-0.00192316	0.00000000	0.00
H12	0.00258304	-0.00117432	0.00069445	0.00
H13	0.00258306	-0.00117428	-0.00069452	0.00
O14	-0.05518561	-0.02502507	0.00000000	0.06
H15	0.87106296	0.41850540	-0.00000001	0.97

Table S1b. Actual and normalized normal mode displacement for strongly/moderately coupled modes ($\xi_{R\sim}$>0.2) with respect to OH stretching mode (target mode) for butanol molecule

Actual normal mode displacement ($\mathbf{q_a^i}$)						
Atom	Mode 39	Mode 18	Mode 13	Mode 5	Mode 3	Mode 1
O14	0.06	0.04	0.12	0.06	0.12	0.00
H15	0.97	0.61	0.21	0.95	0.21	0.15
Normalized normal mode displacement ($\mathbf{q_R}$)						
Atom	Mode 39	Mode 18	Mode 13	Mode 5	Mode 3	Mode 1
O14	1.0	0.6	1.9	0.9	2.0	0.1
H15	1.0	0.6	0.2	1.0	0.2	0.2

One of the target modes for butanol which is studied is mode **39** i.e., O-H stretching where the terminal atom is H15 which shows the maximum displacement in this vibration. To explain a specific instance, the last row of table S1 shows the displacement of H15 atom from the equilibrium position along x, y and z axes respectively. Following that atomic mode displacement, say, q_{H15}^{39} is calculated in unit of length (Å) following eq.1 for H15 atom of mode **39** such that,

$$q_{H15}^{39} = \sqrt{\Delta X_{H15}^2 + \Delta Y_{H15}^2 + \Delta Z_{H15}^2}$$

$$q_{H15}^{39} = \sqrt{(0.87106296)^2 + (0.41850540)^2 + (-0.00000001)^2}$$

$$q_{H15}^{39} = 0.97$$

To assess the position of terminal atom in other modes with respect to the target mode, relative atomic mode displacement 'q_R' is calculated. For that, atomic mode displacements of terminal atom in different modes is required as shown in Table S1b. For illustration, q_R of H15 for mode **5** can be calculated by normalising its displacement with that of H15 in the target mode as,

$$q_R = \frac{q_{H15}^{5}}{q_{H15}^{39}}$$

$$q_R = \frac{0.95}{0.97}$$

q_R = 0.979 and can be calculated similarly for other modes as well.

Categorisation of relative coupling strength (ξ)

We have considered the pair-wise couplings (ξ) of the target mode with the rest of the modes one at a time followed by the computation of the VSCF-PT2. That brings 38 different values of ξ_R which are then compared with the full potential as well as intrinsic anharmonicities. The magnitudes of the individual ξ are different for different pair-wise couplings and the relative coupling values (ξ_R) are distributed from 0.0 to 1.0. For comprehensive categorization of ξ_R values for the strongly, moderately, and weakly coupled modes, we have computed a set of 2,016 different ξ_R values for two molecules, butanol, and NATA molecules. The histogram as given below clearly shows the characteristic distribution pattern of ξ_R. Majority of the ξ_R values are very small and fall in the range of 0.0 to 0.1 (~68%). The second most populated range is 0.2 to 1.0 (~18%). For rest of the cases, the population of vibrational modes decrease systematically with the increase of ξ_R. A small increase in population with ξ_R from 0.9 to 1.0 shows that for each target mode, a group of other modes are always present with very strong mutual coupling. Following this observation, the ξ_R is duly categorized in three different segments: strong ($1.0 \geq \xi_R \geq 0.2$), moderate ($0.1 \leq \xi_R \leq 0.2$) and weak ($\xi_R \leq 0.1$). This classification is followed throughout this work unless it is specified.

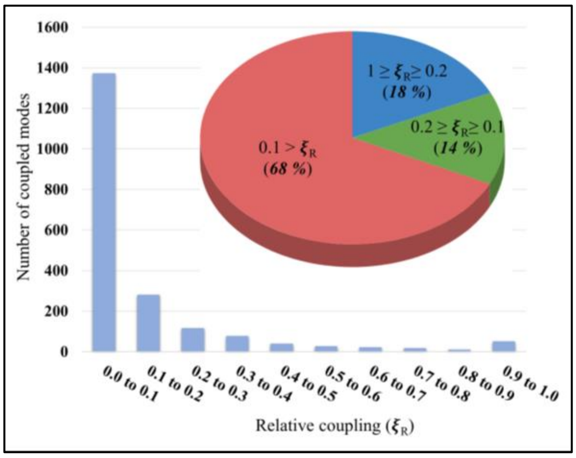

Fig. S2. Histogram for the population/distribution of normal modes following their coupling strengths considering 2016 number of ξ_R values of butanol and NATA molecules. The pie-chart represents the categorization of strongly, moderately, and weakly coupled modes.

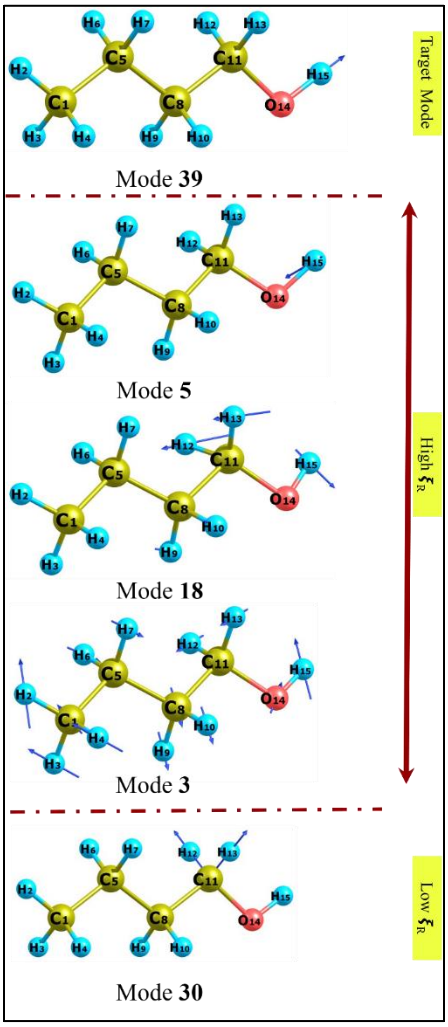

Fig S3. Some selected normal mode of vibrations of butanol. The top panel represents the target mode. Middle and bottom panels represent the strongly and weakly coupled modes, respectively.

Relation between Anharmonic correction and Relative coupling

Below we have plotted the anharmonic corrections due to pure pair wise coupling on top of intrinsic anharmonic values against the ξ_R following the data given in table the main manuscript. A near linear relation is found for $\Delta\upsilon$ against ξ_R for majority of the cases with some exceptions. It is observed that for some cases high ξ_R gives comparatively less/high $\Delta\upsilon$ ($\upsilon_{\text{diagonal}} - \upsilon_{\text{VSCF-PT2}}$) values and sometimes also show blue shifts. Vibrational modes are unique in a sense that for a particular mode, it can vary from one system to another following the topology of the molecular system and the vibrational modes involved in it. Consequently, the extent of coupling, corresponding magnitude, and the direction (red/blue shift) of corrections can vary system to system. However, the overall effect is generally found red shifted towards the converged values. Next, we turn to check the types of modes with different extent of ξ and ξ_R with respect to mode **39**. Mode **5**, corresponds to highest ξ value (so, $\xi_R = 1$), is O14-H15 bending mode which leads to noticeable ~22 cm^{-1} red shift. Mode **3** (torsion, $\xi_R = 0.22$) and **18** (O14-H15 in plane bending + C11-H12H13 bending, $\xi_R = 0.38$) also involve displacements of O14-H15 moiety and strongly coupled with O14-H15 stretching resulting in ~2.7 and ~10.5 cm^{-1} red shifts, respectively. The other 2 strongly/moderately coupled modes i.e., **1** (torsion, $\xi_R = 0.4$) and **13** (O14-H15 bending + CH_2 bending, $\xi_R = 0.19$) result in ~4-6 cm^{-1} red shift. For all these cases, atomic displacement of O-H moiety is found significant. For example, q and q_R for mode **5** are 0.95 and 0.98 and for mode **18**, these are 0.61 and 0.63, respectively. That shows that analysis of q and q_R can offer an efficient protocol to sample a set of important normal modes for a target mode without calculating the full pair-wise PES. Next, the 6 moderately coupled modes mostly involve the bending of this O-H moiety mixed with bending of carbon chain or adjacent -CH_2 groups. These observations also indicate that O-H stretching is mostly a local mode. Rest of the modes are found to be weakly coupled to very weakly coupled and attenuate to $q \approx 0$ with the increase in distance from the target mode (**39**), for which the ξ values are also found very small or close to zero. Overall, it is observed that normal modes corresponding to different types of O-H vibrations are significantly coupled with O-H stretching.

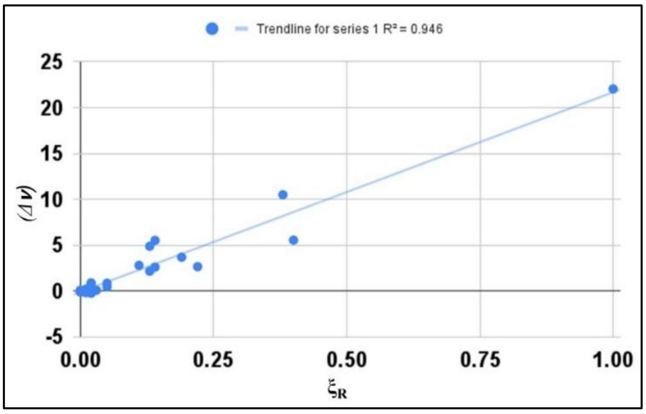

Fig S4. Relation of anharmonic correction and relative coupling with respect to OH stretching mode (mode **39**) for Butanol.

Table S2. Change in O-H stretching frequency ($\nu_{diagonal}$ - $\nu_{VSCF\text{-}PT2}$) of Butanol due to pairwise coupling following sequential addition of rest of the modes.

Description	O-H str. freq. (cm^{-1})	Description	O-H str. freq. (cm^{-1})
v39	3664	**v39,...,19**	3653
v39,38	3664	**v39,...,18**	3642
v39,38,37	3664	**v39,...,17**	3642
v39,38,37,36	3664	**v39,...,16**	3642
v39,...,35	3664	**v39,...,15**	3639
v39,...,34	3664	**v39,...,14**	3639
v39,...,33	3664	**v39,...,13**	3634
v39,...,32	3664	**v39,...,12**	3631
v39,...,31	3664	**v39,...,11**	3632
v39,...,30	3665	**v39,...,10**	3630
v39,...,29	3665	**v39,...,9**	3630
v39,...,28	3665	**v39,...,8**	3630
v39,...,27	3665	**v39,...,7**	3628
v39,...,26	3665	**v39,...,6**	3628
v39,...,25	3665	**v39,...,5**	3610
v39,...,24	3659	**v39,...,4**	3609
v39,...,23	3659	**v39,...,3**	3610
v39,...,22	3658	**v39,...,2**	3610
v39,...,21	3658	**v39,...,1**	3598
v39,...,20	3653		

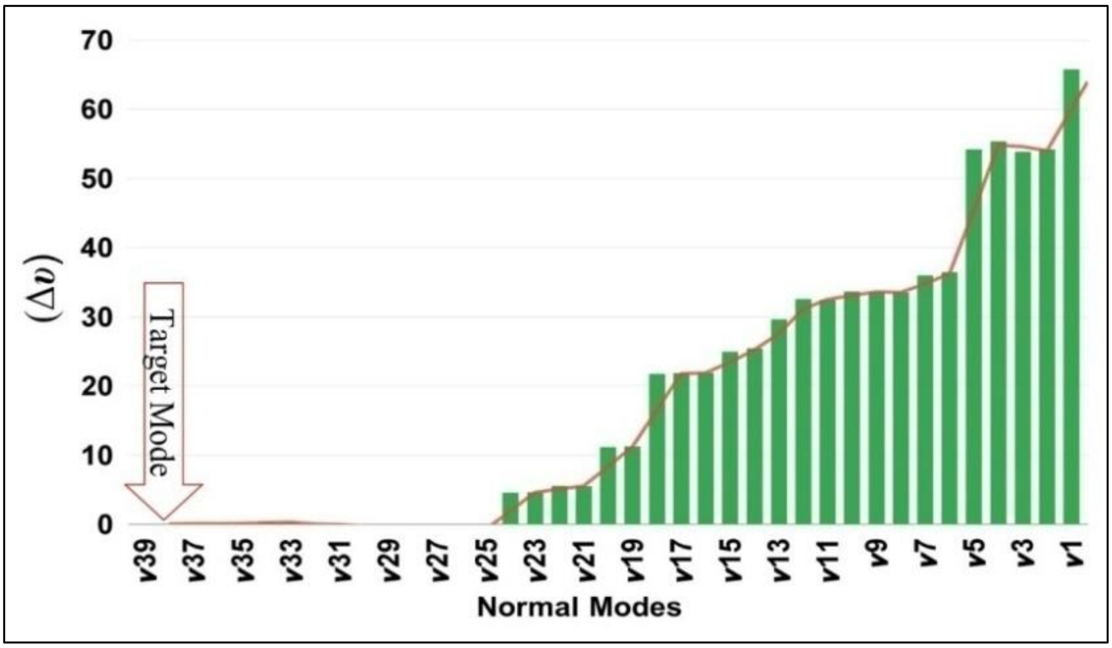

Figure S5. Effects of the addition of sequential normal modes (in descending order) on the O-H stretching (ν_{39}) of butanol. Y-axis represent the change in the wavenumber due to pure pair-wise coupling over diagonal values during sequential addition of normal modes. $\Delta \upsilon = \upsilon_{diagonal} - \upsilon_{VSCF\text{-}PT2}$ (in cm^{-1}) of O-H stretching.

Y-axis represents corrections due to pure pair-wise coupling effects on top of diagonal value (Δυ). X-axis represents the successive addition of normal modes with target mode O-H stretching (*v*39) for the construction of the anharmonic PES. For example, *v*38 and *v*37 represent PESs considering mode **39**, **38** and mode **39**, **38**, **37**, respectively, and so on. It is found that for most of the cases strongly/moderately coupled modes the computed transitions undergo noticeable red shift while contributions of the weakly coupled modes are insignificant.

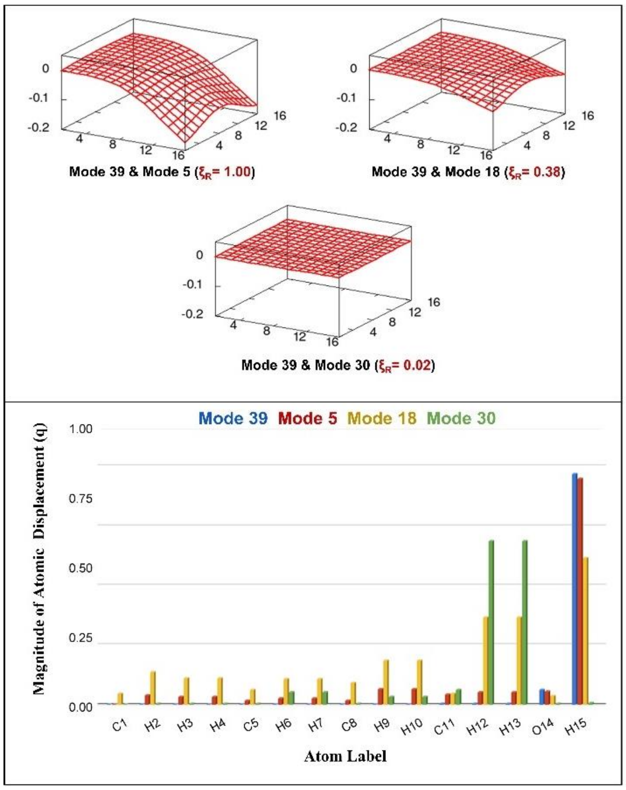

Fig. S6. Pair-wise coupling potentials (V_{ij}^{2coup}) of 3 modes (upper panel) with different magnitude of couplings (ξ) with O-H stretching (mode **39**) for butanol molecule computed at B3LYP/6-311G(*d,p*) using 16×16 grid (these 2D grids map the changes in potential energy as a function of displacement along 2 normal modes) along with their atomic displacement (q) of same modes (lower panel).

Table S3. Comparisons of computed anharmonic frequencies (in cm^{-1}) and intensities (km mol^{-1}) of different VTA guided PESs considering various sets of normal modes by analysing relative normal mode displacement (q_R) and relative coupling (ξ_R) with diagonal and full PES for O-H stretching (mode **39**), O-H bending (mode **18**), CH_3 stretching (Mode **37**) and CH_3 bending (Mode **27**) of butanol. The bold number in PES type represents target mode. Here ω_{HO} and I_{HO} represent corresponding harmonic frequencies (in cm^{-1}) and intensities (km mol^{-1}), respectively.

Mode 39: O-H stretching (ω_{HO}= 3835 cm^{-1}, I_{HO} = 21.13)								
PES type	q_R	υ_{O-H}	I_{O-H}		**PES type**	ξ_R	υ_{O-H}	I_{O-H}
Diagonal		3664	14.1		Diagonal		3664	14.1
39,18,5	≥ 0.5	3632	17.7		**39**,24,20,15,13 12,7	0.1 ≤ ξ_R ≤0.2	3642	14.8
39,20,18,5	≥ 0.4	3628	17.9		**39**,18,5,3,1	≥ 0.2	3613	18.1
39,24,20,18,15,5	≥ 0.3	3622	18.1		**39**,24,20,18,15,13,12,7,5,3,1	≥ 0.1	3602	18.8
39,24,20,18,15,13,12,5,3	≥ 0.2	3615	18.5					
Full PES		3598	18.9		Full PES		3598	18.9
Mode 18: O-H Bending (ω_{HO} = 1250 cm^{-1}, I_{HO} = 44.36)								
PES type	q_R	υ_{O-H}	I_{O-H}		**PES type**	ξ_R	υ_{O-H}	I_{O-H}
Diagonal		1263	45.3		Diagonal		1263	45.3
39,24,20,**18**,5	≥ 0.5	1220	45.1		33,24,22,21,**18**,6	0.1 ≤ ξ_R ≤0.2	1267	45.3
39,24,20,**18**,15,12,5	≥ 0.4	1218	45.1		39,38,36,34,31,30,20,**18**,15,14,13,12,10,7,5,3,1	≥ 0.2	1200	45.0
39,24,20,**18**,15,13,12,5,3	≥ 0.3	1221	45.0		39,38,36,34,33,31,30,24,22,21,20,**18**,15,14,13,12,10,7,6,5,3,1	≥ 0.1	1204	45.0
39,24,22,20,**18**,15,13,12,7,5,3,1	≥ 0.2	1224	45.0					
Full PES		1205	45.0		Full PES		1205	45.0
Mode 37: C-H stretching (ω_{HO} = 3079 cm^{-1}, I_{HO} = 79.01)								
PES type	q_R	υ_{C-H}	I_{C-H}		**PES type**	ξ_R	υ_{C-H}	I_{C-H}
Diagonal		3131	78.8		Diagonal		3131	78.8
38,**37**,34,33,28,27,26,23,11,4	≥ 0.5	2910	76.8		**37**,36,35,28,27,26,25,11,10,9,8	0.1 ≤ ξ_R ≤0.2	3070	78.7
38,**37**,34,33,28,27,26,25,23,15,11,9,4,1	≥ 0.4	2891	76.7		38,**37**,34,33,32,23,4,2,1	≥ 0.2	2925	76.8
38,**37**,36,34,33,28,27,26,25,23,17,15,12,11,10,9,8,6,4,3,1	≥ 0.3	2875	76.6		38,**37**,36,35,34,33,32,28,27,26,25,23,11,10,9,8,4,2,1	≥ 0.1	2876	76.6
38,**37**,36,35,34,33,28,27,26,25,23,21,17,16,15,12,11,10,9,8,6,4,3,2,1	≥ 0.2	2872	76.6					
Full PES		2862	76.6		Full PES		2862	76.6
Mode 27: C-H Bending (ω_{HO} = 1501 cm^{-1}, I_{HO} = 7.6)								
PES type	q_R	υ_{C-H}	I_{C-H}		**PES type**	ξ_R	υ_{C-H}	I_{C-H}
Diagonal		1501	8.0		Diagonal		1501	8.0
38,33,**27**,23,10,4	≥ 0.5	1489	8.0		34,28,**27**,26,4	0.1 ≤ ξ_R ≤0.2	1514	8.0
38,34,33,**27**,23,15,10,4	≥ 0.4	1487	8.0		38,37,**27**	≥ 0.2	1465	8.0
38,34,33,28,**27**,26,23,15,10,4,3,2	≥ 0.3	1492	8.0		38,37,34,28,**27**,26,4	≥ 0.1	1482	8.0
38,34,33,28,**27**,26,23,20,17,15,11,10,7,4,3,2	≥ 0.2	1493	8.0					
Full PES		1480	8.0		Full PES		1480	8.0

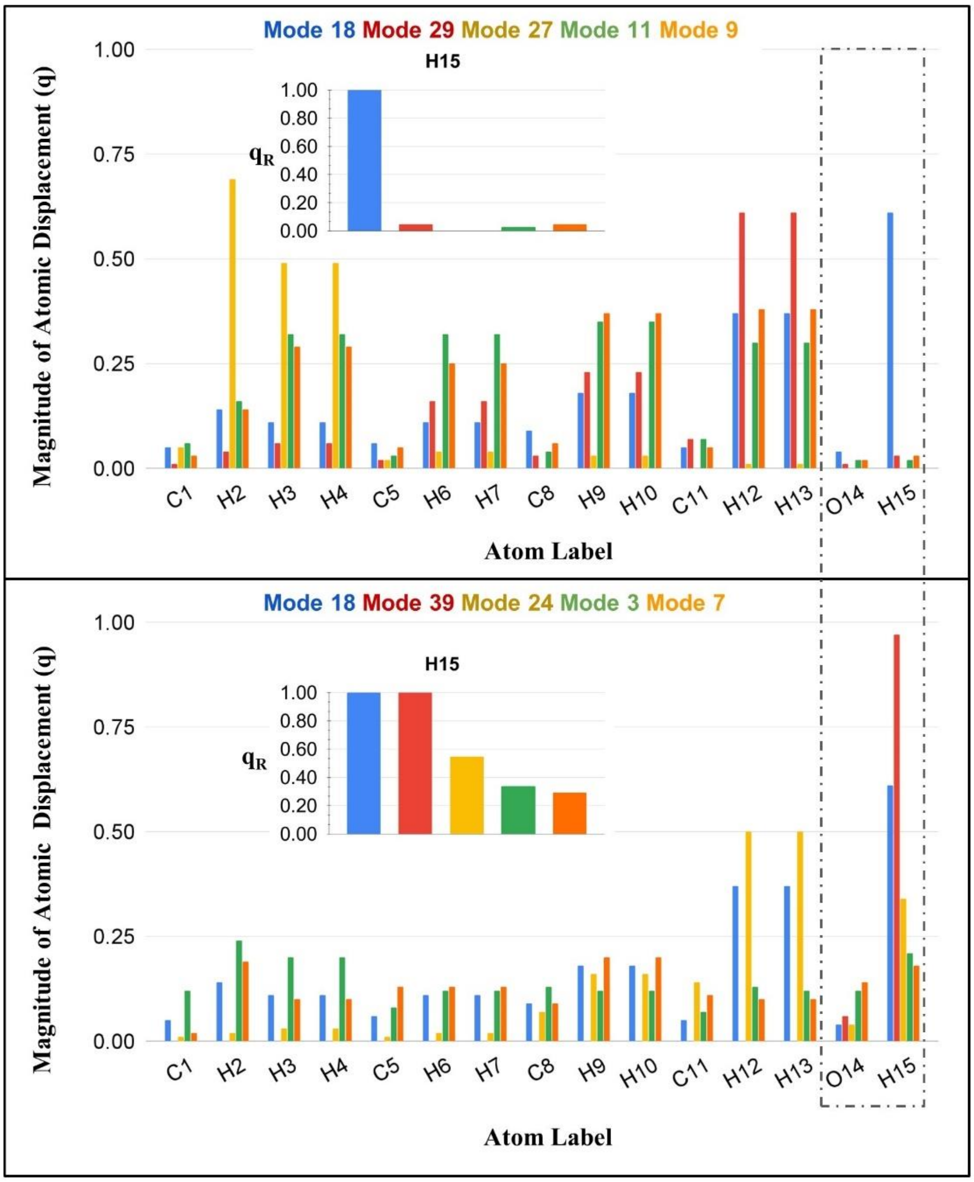

Figure S7. Normal mode analysis of O14-H15 bending (Mode **18**) of butanol. The upper and lower panels represent some weakly coupled and strongly coupled normal modes, respectively, with O-H bending. Displacements during different modes are given in different colors

Table S4. Individual coupling (ξ) and relative coupling (**ξ_R**) strength of O-H in plane bending (ξ_{18}) with rest of the normal modes along with anharmonic corrections ($\Delta\upsilon = \upsilon_{diagonal} - \upsilon_{VSCF\text{-}PT2}$ in cm^{-1}) for butanol.

Pair-wise coupling	ξ	**ξ_R**	Δυ		**Pair-wise coupling**	ξ	**ξ_R**	Δυ
ξ(18,39)	1188	0.85	25.06		ξ(18,20)	324	0.23	-3.73
ξ(18,38)	373	0.27	1.37		ξ(18,19)	49	0.03	-1.63
ξ(18,37)	97	0.07	1.45		ξ(18,17)	52	0.04	-1.01
ξ(18,36)	414	0.30	3.23		ξ(18,16)	108	0.08	-0.64
ξ(18,35)	114	0.08	1.41		ξ(18,15)	349	0.25	-2.28
ξ(18,34)	561	0.40	1.57		ξ(18,14)	299	0.21	0.26
ξ(18,33)	209	0.15	1.89		ξ(18,13)	571	0.41	-4.24
ξ(18,32)	87	0.06	0.24		ξ(18,12)	657	0.47	-1.63
ξ(18,31)	1136	0.81	7.85		ξ(18,11)	29	0.02	-1.12
ξ(18,30)	1395	1.00	4.33		ξ(18,10)	319	0.23	-0.88
ξ(18,29)	27	0.02	-0.2		ξ(18,9)	73	0.05	-1.6
ξ(18,28)	69	0.05	-0.14		ξ(18,8)	60	0.04	-0.72
ξ(18,27)	60	0.04	-0.13		ξ(18,7)	485	0.35	-3.48
ξ(18,26)	31	0.02	-0.2		ξ(18,6)	240	0.17	-0.15
ξ(18,25)	91	0.07	-0.05		ξ(18,5)	526	0.38	-16.8
ξ(18,24)	242	0.17	-4.25		ξ(18,4)	59	0.04	-1.39
ξ(18,23)	101	0.07	-0.54		ξ(18,3)	554	0.40	-3.8
ξ(18,22)	228	0.16	-1.07		ξ(18,2)	112	0.08	-0.31
ξ(18,21)	139	0.10	-0.48		ξ(18,1)	1186	0.85	-2.63

Table S5. Individual coupling (ξ) and relative coupling **(**ξ_R) strength of CH_3 stretching (ξ_{37}) with rest of the normal modes along with anharmonic corrections ($\Delta \upsilon = \upsilon_{diagonal} - \upsilon_{VSCF\text{-}PT2}$ in cm^{-1})   for butanol.

Pair-wise Coupling	ξ	ξ_R	$\Delta\upsilon$	**Pair-wise coupling**	ξ	ξ_R	$\Delta\upsilon$
ξ(37,39)	1	0.00	0.01	ξ(37,19)	136	0.02	1.14
ξ(37,38)	6377	0.77	-5.93	ξ(37,18)	97	0.01	1.53
ξ(37,36)	1440	0.17	-9.12	ξ(37,17)	657	0.08	5.01
ξ(37,35)	1254	0.15	-8.87	ξ(37,16)	423	0.05	3.16
ξ(37,34)	8262	1.00	36.13	ξ(37,15)	684	0.08	5.92
ξ(37,33)	7648	0.93	46.23	ξ(37,14)	34	0.00	0.25
ξ(39,32)	1900	0.23	7.07	ξ(37,13)	109	0.01	0.91
ξ(37,31)	244	0.03	-0.35	ξ(37,12)	156	0.02	1.01
ξ(37,30)	70	0.01	-0.65	ξ(37,11)	1259	0.15	10.24
ξ(37,29)	21	0.00	0.65	ξ(37,10)	982	0.12	8.35
ξ(37,28)	1021	0.12	10.96	ξ(37,9)	1185	0.14	9.7
ξ(37,27)	1366	0.17	11.17	ξ(37,8)	1113	0.13	9.51
ξ(37,26)	1464	0.18	11.19	ξ(37,7)	248	0.03	1.9
ξ(37,25)	846	0.10	5.91	ξ(37,6)	209	0.03	1.45
ξ(37,24)	40	0.00	0.26	ξ(37,5)	50	0.01	0.14
ξ(37,23)	1949	0.24	20.11	ξ(37,4)	4688	0.57	59.12
ξ(37,22)	412	0.05	3.12	ξ(37,3)	560	0.07	4.29
ξ(37,21)	376	0.05	3.26	ξ(37,2)	2594	0.31	25.14
ξ(37,20)	79	0.01	2.33	ξ(37,1)	2631	0.32	23.06

Table S6. Individual coupling (ξ) and relative coupling (**ξ_R**) strength of C-H bending (ξ_{27}) with rest of the normal modes along with anharmonic corrections ($\Delta\upsilon = \upsilon_{diagonal} - \upsilon_{VSCF\text{-}PT2}$ cm^{-1}) for butanol.

Pair-wise coupling	**ξ**	**ξ_R**	**Δ*υ***		**Pair-wise coupling**	**ξ**	**ξ_R**	**Δ*υ***
ξ(27,39)	2	0.00	0.02		ξ(27,19)	9	0.00	-0.06
ξ(27,38)	3891	1.00	23.56		ξ(27,18)	60	0.02	-0.09
ξ(27,37)	1366	0.35	10.83		ξ(27,17)	19	0.00	-0.5
ξ(27,36)	131	0.03	1.28		ξ(27,16)	14	0.00	-0.29
ξ(27,35)	78	0.02	0.69		ξ(27,15)	41	0.01	-0.83
ξ(27,34)	685	0.18	2.76		ξ(27,14)	22	0.01	0.16
ξ(27,33)	198	0.05	8.38		ξ(27,13)	3	0.00	-0.05
ξ(27,32)	46	0.01	0.66		ξ(27,12)	28	0.01	-0.06
ξ(27,31)	1	0.00	0.01		ξ(27,11)	51	0.01	-1.06
ξ(27,30)	3	0.00	0.04		ξ(27,10)	65	0.02	-1.57
ξ(27,29)	68	0.02	0.06		ξ(27,9)	60	0.02	-0.92
ξ(27,28)	448	0.12	0.43		ξ(27,8)	18	0.00	-0.37
ξ(27,26)	520	0.13	0.54		ξ(27,7)	40	0.01	-0.44
ξ(27,25)	334	0.09	0.12		ξ(27,6)	67	0.02	-0.34
ξ(27,24)	8	0.00	0		ξ(27,5)	10	0.00	-0.05
ξ(27,23)	105	0.03	-0.08		ξ(27,4)	388	0.10	-17.64
ξ(27,22)	90	0.02	0.12		ξ(27,3)	55	0.01	-0.83
ξ(27,21)	4	0.00	-0.07		ξ(27,2)	326	0.08	-6.11
ξ(27,20)	50	0.01	-0.04		ξ(27,1)	101	0.03	-0.4

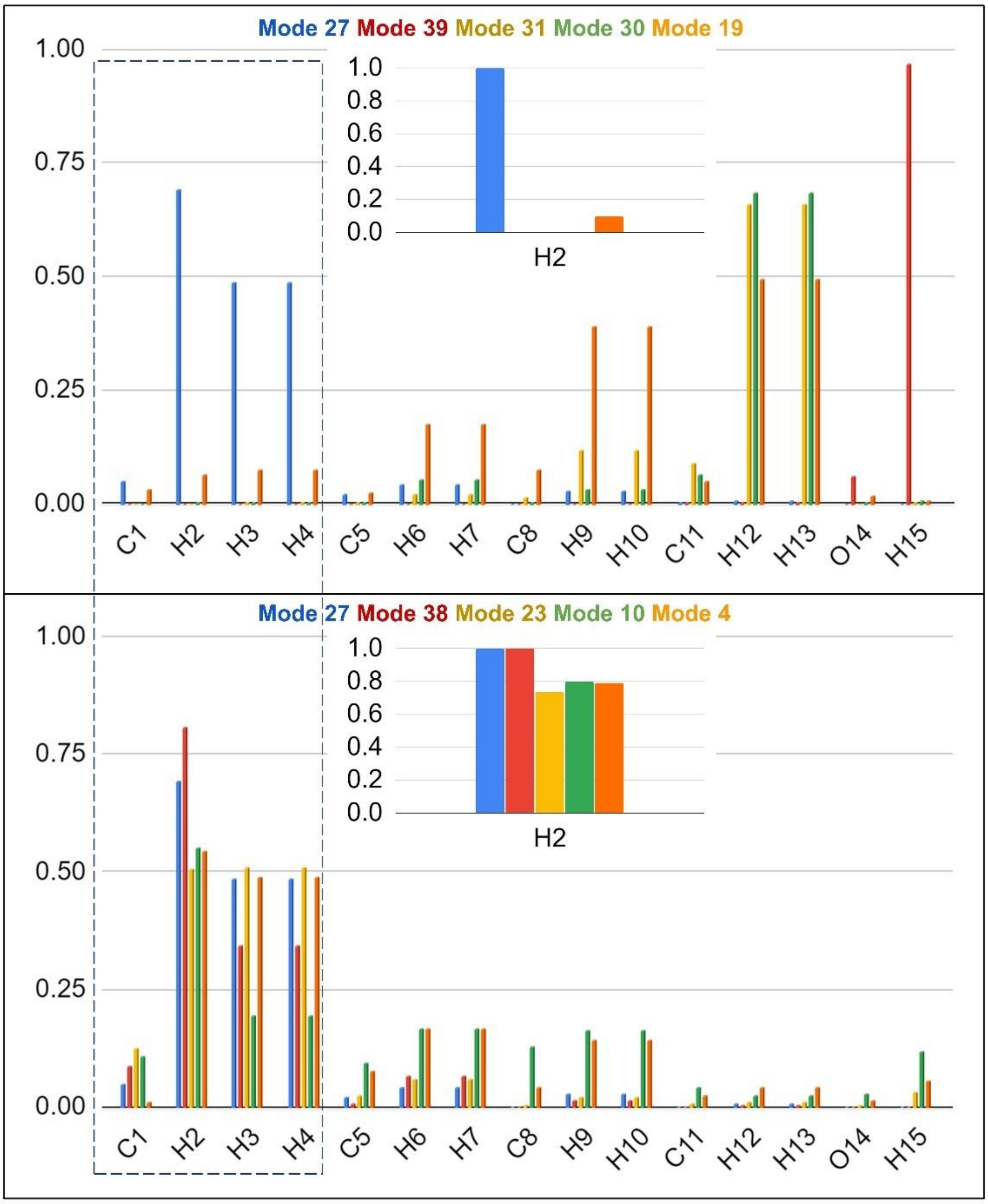

Figure S8. Normal mode analysis of C1-H2H3H4 bending (Mode **27**) of butanol. The upper and lower panels represent some weakly coupled and strongly coupled normal modes, respectively, with C-H bending. Displacements during different modes are given in different colors.

Table S7. Comparative study of different relative coupling (ξ_R) values for Mode **39** (O-H stretching), Mode **37** (CH_3 stretching), Mode **18** (O-H bending) and Mode **27** (CH_3 bending) of Butanol. Some selected normal modes of different relative coupling values are considered.

O-H str. (Mode 39)			**O-H bend** [O-H in plane bend, CH2 bend (H12-C11-H13)] **(Mode 18)**			**C-H str.** [CH2 str. (H4-C1-H3)] **(Mode 37)**			**C-H bend** C1-H2-H3-H4 bending **(Mode 27)**		
Mode	ξ	ξ_R	**Mode**	ξ	ξ_R	**Mode**	ξ	ξ_R	**Mode**	ξ	ξ_R
5	3092	1.00	**30**	1395	1.00	**34**	8262	1.00	**38**	3891	1.00
O-H out of plane bending			CH_2 symmetric. Str. (H12-C11H13)			CH_2 symmetric. str (H9-C8-H10, CH3 str.)			CH_3 anti-symmetric. Str.		
18	1188	0.38	**39**	1188	0.85	**33**	7648	0.93	**37**	1366	0.35
O-H in plane bend, CH_2 bend (H12-C11-H13)			O-H str.			CH_2 symmetric. str (H9-C8-H10, CH3 str.			CH_3 symmetric. Str. (H3-C1-H4)		
13	572	0.19	**31**	1136	0.81	**38**	6377	0.77	**34**	685	0.18
O-H in plane bending, H10-C8-H9 bending			CH_2 anti-symmetric. str (H12-C11H13)			CH_3 anti-symmetric. str.			CH_2 symmetric. str (H9-C8-H10, C H3 str.)		
20	422	0.14	**13**	571	0.41	**4**	4688	0.57	**26**	520	0.13
O-H in plane bending, C5-H6-H7 bending, C8-H9-H10 bending			O-H in plane bending, CH_2 bending (H9-C8-H10)			CH_3 twisting			CH_2 scissoring (H9-C8H10)		
24	396	0.13	**15**	349	0.25	**32**	1900	0.23	**28**	448	0.12
O-H in plane bending, CH_2 bending (H12-C11-H13)			O-H in plane bending, CH_3 bending, CH_2 bending (H3-C1-H4, H6C5-H7, H12-C11-H13)			CH_2 symmetric. str. (H6-C5-H7)			CH_3, CH_2, CH_2 and CH_2 scissoring		
12	410	0.13	**24**	242	0.17	**23**	1949	0.24	**4**	388	0.10
C1-C5 str., C8-C11 str., O-H in bending			O-H in plane bending, H12C11-H13 bending			CH_3 bending			CH_3 twisting		
15	342	0.11	**32**	87	0.06	**26**	1464	0.18	**25**	334	0.09
C5-C8 str., O-H in plane bending, CH_3 bending			CH_2 symmetric. Str. (H6-C5-H7)			CH_3 and CH_2 scissoring, (H9-C8H10)			CH_3, C1-H2-H3-H4, C5-H6-H7 and C8-H9-H10scissoring		
37	1	0.00	**37**	97	0.07	**36**	1440	0.17	**2**	326	0.08
CH_2 str. (H4-C1-H3)			CH_3 symmetric. Str. (H3-C1-H4)			CH_2 anti-symmetric. str (H9-C8-H10)			Chain Torsional mode		
36	1	0.00	**11**	29	0.02	**30**	70	0.01	**33**	198	0.05
CH_2 str. (H9-C8-H10)			CH_3 twisting, CH_2 twisting (H6-C5-H7, H9-C8-H10, H12-C11-H13)			CH_2 symmetric. str (H12-C11H13)			CH_2 symmetric. str (H9-C8-H10, CH3 str.		
35	10	0.00	**27**	60	0.04	**13**	109	0.01	**23**	105	0.03
CH_2 str. (H6-C5-H7)			CH_3 bending			O-H in plane bending, CH_2 bending (H9-C8-H10)			CH_3 bending		

For example, the strongest coupling with O-H stretching is O-H out-of-plane bending (mode **5,** ξ_R = 1.0) followed by chain torsion (mode **1**, ξ_R = 0.40). Further, mode **18**, which is O-H in-plane + CH_2 (H12-C11-H13) bending of immediate neighbor posit strong coupling (ξ_R = 0.38) while mode **20** which is O-H + next two -CH_2 (H9-C8-H10 + H6-C5-H7) bending posits weak coupling ($\xi_R \approx 0.0$) due to spacing out from each other.

Table S8. Individual (ξ); relative coupling (ξ_R) strengths of anti-symmetric N-H stretching (mode **92**) with rest of the normal modes for NATA (three smallest torsional modes are excluded for numerical stability).

Modes	ξ	ξ_R	Modes	ξ	ξ_R
93	27461	1.00	**48**	3	0.00
	---	---	**47**	82	0.00
91	6983	0.25	**46**	3	0.00
90	20542	0.75	**45**	13	0.00
89	28	0.00	**44**	4	0.00
88	5	0.00	**43**	26	0.00
87	11	0.00	**42**	336	0.01
86	4	0.00	**41**	18	0.00
85	2	0.00	**40**	172	0.01
84	27	0.00	**39**	1927	0.07
83	7	0.00	**38**	257	0.01
82	68	0.00	**37**	299	0.01
81	19	0.00	**36**	1573	0.06
80	3	0.00	**35**	935	0.03
79	75	0.00	**34**	68	0.00
78	120	0.00	**33**	172	0.01
77	170	0.01	**32**	300	0.01
76	39	0.00	**31**	128	0.00
75	2341	0.09	**30**	149	0.01
74	33	0.00	**29**	307	0.01
73	2	0.00	**28**	120	0.00
72	175	0.01	**27**	280	0.01
71	112	0.00	**26**	2465	0.09
70	9	0.00	**25**	84	0.00
69	7	0.00	**24**	338	0.01
68	6	0.00	**23**	665	0.02
67	0	0.00	**22**	1231	0.04
66	312	0.01	**21**	454	0.02
65	24	0.00	**20**	219	0.01
64	282	0.01	**19**	118	0.00
63	120	0.00	**18**	141	0.01
62	110	0.00	**17**	137	0.00
61	31	0.00	**16**	53	0.00
60	78	0.00	**15**	84	0.00
59	71	0.00	**14**	143	0.01
58	5	0.00	**13**	71	0.00
57	1686	0.06	**12**	172	0.01
56	23	0.00	**11**	455	0.02
55	140	0.01	**10**	67	0.00
54	93	0.00	**9**	172	0.01
53	9	0.00	**8**	300	0.01
52	2	0.00	**7**	128	0.00
51	9	0.00	**6**	149	0.01
50	27	0.00	**5**	307	0.01
49	34	0.00	**4**	120	0.00

Table S9. Individual (ξ) and relative (ξ_R) coupling strength of symmetric N-H stretching (ξ_{90}) with rest of the normal modes for NATA molecule.

Mode	ξ	ξ_R	Mode	ξ	ξ_R	Mode	ξ	ξ_R
93	1453	0.07	**63**	179	0.01	**33**	8203	0.40
92	20542	1.00	**62**	125	0.01	**32**	1101	0.05
91	608	0.03	**61**	64	0.00	**31**	1049	0.05
90	--	--	**60**	171	0.01	**30**	7296	0.36
89	23	0.00	**59**	22	0.00	**29**	5109	0.25
88	12	0.00	**58**	495	0.02	**28**	226	0.01
87	19	0.00	**57**	36	0.00	**27**	375	0.02
86	13	0.00	**56**	297	0.01	**26**	1331	0.06
85	11	0.00	**55**	29	0.00	**25**	218	0.01
84	140	0.01	**54**	83	0.00	**24**	911	0.04
83	43	0.00	**53**	42	0.00	**23**	1213	0.06
82	34	0.00	**52**	18	0.00	**22**	846	0.04
81	22	0.00	**51**	5995	0.29	**21**	1388	0.07
80	5	0.00	**50**	99	0.00	**20**	9334	0.45
79	357	0.02	**49**	21	0.00	**19**	130	0.01
78	391	0.02	**48**	76	0.00	**18**	70	0.00
77	829	0.04	**47**	13	0.00	**17**	406	0.02
76	29	0.00	**46**	9	0.00	**16**	4918	0.24
75	8103	0.39	**45**	102	0.00	**15**	769	0.04
74	14	0.00	**44**	93	0.00	**14**	223	0.01
73	52	0.00	**43**	60	0.00	**13**	301	0.01
72	578	0.03	**42**	11	0.00	**12**	736	0.04
71	3	0.00	**41**	409	0.02	**11**	11	0.00
70	120	0.01	**40**	11	0.00	**10**	643	0.03
69	57	0.00	**39**	30	0.00	**9**	352	0.02
68	46	0.00	**38**	4	0.00	**8**	225	0.01
67	7	0.00	**37**	91	0.00	**7**	418	0.02
66	42	0.00	**36**	1850	0.09	**6**	1264	0.06
65	86	0.00	**35**	124	0.01	**5**	479	0.02
64	240	0.01	**34**	915	0.04	**4**	522	0.03

Table S10. Individual (ξ) and relative (ξ_R) coupling strength of φ NH stretching (ξ_{91}) with rest of the normal modes for NATA molecule.

Mode	ξ	ξ_R	Mode	ξ	ξ_R	Mode	ξ	ξ_R
93	2641	0.38	**63**	4	0.00	**33**	57	0.01
92	6983	1.00	**62**	56	0.01	**32**	38	0.01
91	--	--	**61**	17	0.00	**31**	29	0.00
90	608	0.09	**60**	178	0.03	**30**	48	0.01
89	48	0.01	**59**	7	0.00	**29**	43	0.01
88	78	0.01	**58**	460	0.07	**28**	1438	0.21
87	32	0.00	**57**	70	0.01	**27**	34	0.00
86	101	0.01	**56**	755	0.11	**26**	17	0.00
85	152	0.02	**55**	179	0.03	**25**	15	0.00
84	497	0.07	**54**	45	0.01	**24**	19	0.00
83	59	0.01	**53**	14	0.00	**23**	559	0.08
82	19	0.00	**52**	47	0.01	**22**	1703	0.24
81	58	0.01	**51**	62	0.01	**21**	873	0.13
80	184	0.03	**50**	62	0.01	**20**	202	0.03
79	229	0.03	**49**	7	0.00	**19**	21	0.00
78	1	0.00	**48**	45	0.01	**18**	44	0.01
77	100	0.01	**47**	4	0.00	**17**	82	0.01
76	38	0.01	**46**	22	0.00	**16**	45	0.01
75	46	0.01	**45**	51	0.01	**15**	45	0.01
74	26	0.00	**44**	133	0.02	**14**	140	0.02
73	13	0.00	**43**	158	0.02	**13**	24	0.00
72	700	0.10	**42**	21	0.00	**12**	45	0.01
71	2	0.00	**41**	8	0.00	**11**	19	0.00
70	166	0.02	**40**	63	0.01	**10**	50	0.01
69	103	0.01	**39**	15	0.00	**9**	12	0.00
68	9	0.00	**38**	27	0.00	**8**	65	0.01
67	42	0.01	**37**	31	0.00	**7**	91	0.01
66	53	0.01	**36**	43	0.01	**6**	396	0.06
65	50	0.01	**35**	20	0.00	**5**	242	0.03
64	140	**0.02**	**34**	113	0.02	**4**	31	0.00

Table S11. Individual (ξ) and relative (ξ_R) coupling strength of Indole N-H stretching (ξ_{93}) with rest of the normal modes for NATA molecule.

Mode	ξ	ξ_R		Mode	ξ	ξ_R		Mode	ξ	ξ_R
93	--	--		**63**	142	0.01		**33**	44	0.00
92	27461	1.00		**62**	153	0.01		**32**	18	0.00
91	2641	0.10		**61**	116	0.00		**31**	17	0.00
90	1497	0.05		**60**	88	0.00		**30**	73	0.00
89	3161	0.12		**59**	202	0.01		**29**	56	0.00
88	24	0.00		**58**	79	0.00		**28**	7	0.00
87	44	0.00		**57**	350	0.01		**27**	176	0.01
86	124	0.00		**56**	8	0.00		**26**	389	0.01
85	5	0.00		**55**	103	0.00		**25**	111	0.00
84	2	0.00		**54**	237	0.01		**24**	19	0.00
83	1	0.00		**53**	26	0.00		**23**	55	0.00
82	81	0.00		**52**	18	0.00		**22**	83	0.00
81	10	0.00		**51**	150	0.01		**21**	88	0.00
80	4	0.00		**50**	45	0.00		**20**	546	0.02
79	2	0.00		**49**	258	0.01		**19**	219	0.01
78	27	0.00		**48**	368	0.01		**18**	1140	0.04
77	7	0.00		**47**	2	0.00		**17**	2044	0.07
76	183	0.01		**46**	4	0.00		**16**	1296	0.05
75	57	0.00		**45**	35	0.00		**15**	808	0.03
74	94	0.00		**44**	61	0.00		**14**	148	0.01
73	106	0.00		**43**	17	0.00		**13**	187	0.01
72	21	0.00		**42**	18	0.00		**12**	37	0.00
71	321	0.01		**41**	37	0.00		**11**	386	0.01
70	4	0.00		**40**	16	0.00		**10**	22	0.00
69	60	0.00		**39**	63	0.00		**9**	23	0.00
68	24	0.00		**38**	41	0.00		**8**	106	0.00
67	3	0.00		**37**	29	0.00		**7**	16	0.00
66	555	0.02		**36**	50	0.00		**6**	19	0.00
65	6	0.00		**35**	52	0.00		**5**	207	0.01
64	109	0.00		**34**	44	0.00		**4**	8	0.00

Table S12. Individual (ξ) and relative (ξ_R) coupling strength of C=O stretching (ξ_{78}) with rest of the normal modes for NATA molecule.

Mode	ξ	ξ_R	Mode	ξ	ξ_R	Mode	ξ	ξ_R
93	27	0.01	**63**	1013	0.46	**33**	461	0.21
92	120	0.05	**62**	417	0.19	**32**	150	0.07
91	1	0.00	**61**	11	0.00	**31**	409	0.19
90	391	0.18	**60**	410	0.19	**30**	288	0.13
89	24	0.01	**59**	177	0.08	**29**	193	0.09
88	4	0.00	**58**	422	0.19	**28**	31	0.01
87	9	0.00	**57**	191	0.09	**27**	135	0.06
86	6	0.00	**56**	438	0.20	**26**	152	0.07
85	8	0.00	**55**	173	0.08	**25**	49	0.02
84	13	0.01	**54**	487	0.22	**24**	87	0.04
83	3	0.00	**53**	144	0.07	**23**	450	0.20
82	34	0.02	**52**	100	0.05	**22**	59	0.03
81	17	0.01	**51**	2200	1.00	**21**	215	0.10
80	7	0.00	**50**	10	0.00	**20**	762	0.35
79	145	0.07	**49**	104	0.05	**19**	48	0.02
78	--	--	**48**	172	0.08	**18**	16	0.01
77	220	0.10	**47**	67	0.03	**17**	30	0.01
76	38	0.02	**46**	37	0.02	**16**	504	0.23
75	1158	0.53	**45**	141	0.06	**15**	74	0.03
74	14	0.01	**44**	264	0.12	**14**	185	0.08
73	118	0.05	**43**	361	0.16	**13**	63	0.03
72	352	0.16	**42**	8	0.00	**12**	187	0.08
71	4	0.00	**41**	194	0.09	**11**	113	0.05
70	12	0.01	**40**	12	0.01	**10**	99	0.04
69	84	0.04	**39**	65	0.03	**9**	130	0.06
68	233	0.11	**38**	4	0.00	**8**	103	0.05
67	24	0.01	**37**	108	0.05	**7**	30	0.01
66	14	0.01	**36**	471	0.21	**6**	75	0.03
65	11	0.01	**35**	69	0.03	**5**	1282	0.58
64	781	0.35	**34**	28	0.01	**4**	32	0.01

Table S13. Individual (ξ) and relative (ξ_R) coupling strength of NH_2 bending (ξ_{51}) with rest of the normal modes for NATA molecule.

Mode	ξ	ξ_R	Mode	ξ	ξ_R	Mode	ξ	ξ_R
93	150	0.03	**63**	221	0.04	**33**	491	0.08
92	1686	0.28	**62**	415	0.07	**32**	126	0.02
91	62	0.01	**61**	8	0.00	**31**	174	0.03
90	5995	1.00	**60**	561	0.09	**30**	331	0.06
89	34	0.01	**59**	88	0.01	**29**	91	0.02
88	11	0.00	**58**	2421	0.40	**28**	16	0.00
87	8	0.00	**57**	23	0.00	**27**	178	0.03
86	12	0.00	**56**	141	0.02	**26**	142	0.02
85	10	0.00	**55**	52	0.01	**25**	25	0.00
84	19	0.00	**54**	106	0.02	**24**	156	0.03
83	9	0.00	**53**	54	0.01	**23**	183	0.03
82	34	0.01	**52**	70	0.01	**22**	185	0.03
81	203	0.03	**51**	--	--	**21**	487	0.08
80	2	0.00	**50**	61	0.01	**20**	612	0.10
79	330	0.06	**49**	126	0.02	**19**	54	0.01
78	2200	0.37	**48**	99	0.02	**18**	28	0.00
77	71	0.01	**47**	39	0.01	**17**	142	0.02
76	32	0.01	**46**	28	0.00	**16**	327	0.05
75	744	0.12	**45**	125	0.02	**15**	378	0.06
74	56	0.01	**44**	33	0.01	**14**	50	0.01
73	132	0.02	**43**	33	0.01	**13**	175	0.03
72	70	0.01	**42**	4	0.00	**12**	299	0.05
71	2	0.00	**41**	140	0.02	**11**	8	0.00
70	24	0.00	**40**	4	0.00	**10**	58	0.01
69	25	0.00	**39**	20	0.00	**9**	227	0.04
68	23	0.00	**38**	11	0.00	**8**	27	0.00
67	3	0.00	**37**	36	0.01	**7**	75	0.01
66	36	0.01	**36**	96	0.02	**6**	86	0.01
65	39	0.01	**35**	12	0.00	**5**	1286	0.21
64	2129	0.36	**34**	34	0.01	**4**	22	0.00

Table S14. Comparative study of ξ_{max} for selected N-H stretching, N-H bending and C=O stretching for NATA molecule.

Target Mode (ω)	**Mode with maximum coupling**	ξ_{max}
93 (3684)	92	27461
92 (3683)	93	27461
91 (3599)	92	6983
90 (3473)	92	20542
51 (1135)	90	5995
78 (1755)	51	2200
77 (1714)	58	2677

Table S15. Comparisons of computed anharmonic frequencies (in cm^{-1}) and intensities (km mol^{-1}) of different VTA guided PESs considering various sets of normal modes by analysing relative atomic displacement (q_R) and relative coupling (ξ_R) with diagonal and full PES for Symmetric-NH stretching (Mode **90**), φ N-H (Mode **91**), Anti-symmetric- NH_2 (Mode **92**), Indole N-H stretching (Mode **93**), C=O stretching (Mode **78**), NH_2 bending (Mode **51**), and C=O stretching (Mode **77**) for NATA molecule. The bold number in PES type represent target mode. Here ω_{HO} and I_{HO} represents corresponding harmonic frequencies (in cm^{-1}) and intensities (km mol^{-1}), respectively.

Mode 90: Symmetric NH stretching (ω_{HO} = 3473 cm^{-1}, I_{HO} = 144.5)								
PES type	**q_R**	***υ_{N-H}***	***I_{N-H}***		**PES type**	**ξ_R**	***υ_{N-H}***	***I_{N-H}***
Diagonal		3359	156.4		Diagonal		3359	156.4
90,75,51,33,30	≥ 0.5	3338	151.2		92,**90**,75,51,33,30,29,20,16	≥ 0.2	3235	150.3
90,75,51,33,30	≥ 0.4	3338	151.2		92,**90**,75,51,36,33,30,29,20,16	≥ 0.1	3235	150.1
92,**90**,75,51,33,30,29,20	≥ 0.3	3257	151.6		93,92,**90**,75,51,36,33,32,31,30,29,26,23,21,20,16,6	≥ 0.05	3220	152.5
92,**90**,75,51,36,33,30,29,21,20,16,15	≥ 0.2	3234	149.6		93,92,91,**90**,77,75,72,51,36,34,33,32,31,30,29,26,24,23,22,21,20,16,15,12,10,6,4	≥ 0.03	3217	150.8
Full PES		3255	147.8		Full PES		3255	147.8
Mode 91: φ N-H stretching (ω_{HO}= 3599 cm^{-1}, I_{HO} = 159.3)								
PES type	**q_R**	***υ_{N-H}***	***I_{N-H}***		**PES type**	**ξ_R**	***υ_{N-H}***	***I_{N-H}***
Diagonal		3446	166.2		Diagonal		3446	166.2
91,72,28,22	≥ 0.5	3414	162.7		93,92,**91**,28,22	≥ 0.2	3418	163.4
91,72,58,56,28,22	≥ 0.4	3402	162.2		93,92,**91**,72,56,28,22,21	≥ 0.1	3402	161.8
91,72,58,56,28,22,21	≥ 0.3	3396	161.7		93,92,**91,**90,84,72,58,56,28,23,22,21,6	≥ 0.05	3397	161.2
91,72,70,60,58,56,28,23,22,21,20	≥ 0.2	3387	161.2		93,92,**91,**90,84,80,79,72,60,58,56,55,28,23,22,21,20,6,5	≥ 0.03	3387	160.8
Full PES		3394	160.8		Full PES		3394	160.8
Mode 92: Anti-symmetric NH_2 stretching (ω_{HO} = 3683 cm^{-1}, I_{HO} = 67.6)								
PES type	**q_R**	***υ_{N-H}***	***I_{N-H}***		**PES type**	**ξ_R**	***υ_{N-H}***	***I_{N-H}***
Diagonal		3651	62.8		Diagonal		3651	62.8
92,75,20,16	≥ 0.5	3517	64.7		93,**92**,91,90	≥ 0.2	3532	62.9
92,90,75,51,33,20,16	≥ 0.4	3472	64.8		93,**92**,91,90,75,20	≥ 0.1	3493	64.1
92,90,75,58,51,33,30,20,16	≥ 0.3	3463	64.7		93,**92**,91,90,75,51,33,30,20	≥ 0.05	3465	64.1
92,90,75,64,60,58,51,33,31,30,29,21,20,16,12	≥ 0.2	3453	64.8		93,**92**,91,90,75,51,33,30,29,20,16	≥ 0.03	3449	64.9
Full PES		3455	64.6		Full PES		3455	64.6
Mode 93: Indole N-H stretching (ω_{HO} = 3684 cm^{-1}, I_{HO} = 93.8)								
PES type	**q_R**	***υ_{N-H}***	***I_{N-H}***		**PES type**	**ξ_R**	***υ_{N-H}***	***I_{N-H}***
Diagonal		3556	84.7		Diagonal		3556	84.7
93,17	≥ 0.5	3526	87.2		**93**,92	≥ 0.2	3543	84.1
93,66,17	≥ 0.4	3521	87.6		**93**,92,91,89	≥ 0.1	3544	84.1
93,66,57,49,48,26,18,17	≥ 0.3	3494	88.5		**93**,92,91,90,89,17,16	≥ 0.05	3509	87.0
93,71,66,62,57,55,54,49,48,26,19,18,17,16	≥ 0.2	3485	89.2		**93**,92,91,90,89,18,17,16,15	≥ 0.03	3491	87.7

93, 92, 76, 74, 71, 66, 62, 59, 57, 55, 54, 53, 49, 48, 44, 39, 27, 26, 25, 19, 18, 17, 16, 15, 11	≥ 0.1	3441	89.3					
Full PES		3452	89.2		Full PES		3452	89.2
Mode 78: C=O stretching (ω_{HO} = 1755 cm^{-1}, I_{HO} = 400.5)								
PES type	q_R	$\upsilon_{C=O}$	$I_{C=O}$		**PES type**	ξ_R	$\upsilon_{C=O}$	$I_{C=O}$
Diagonal		1750	396.0		Diagonal		1750	396.0
78,51,23,21,15,14,13,9,6,5	≥ 0.5	1737	395.8		**78**,75,64,63,56,54,51,36,33,23,20,16,5	≥ 0.2	1738	396.2
78,51,33,27,23,21,15,14,13,9,6,5	≥ 0.4	1735	395.9		90,**78**,77,75,72,68,64,63,62,60,58,56,54,51,44,43,36,33,31,30,23,21,20,16,5	≥ 0.1	1731	396.6
78,51,36,33,31,30,27,23,21,15,14,13,12,10,9,8,7,6,5,4	≥ 0.3	1732	396.0					
78,75,51,36,33,31,30,29,27,26,24,23,22,21,20,16,15,14,13,12,10,9,8,7,6,5,4	≥ 0.2	1733	396.3					
Full PES		1723	396.8		Full PES		1723	396.8
Mode 51: NH_2 bending (ω_{HO} = 1135 cm^{-1}, I_{HO} = 0.85)								
PES type	q_R	υ_{N-H}	I_{N-H}		**PES type**	ξ_R	υ_{N-H}	I_{N-H}
Diagonal		1147	0.8		Diagonal		1147	0.8
92,90,75,**51**,33,30,29,20	≥ 0.5	1118	0.8		92,90,78,64,58,**51**,5	≥ 0.2	1115	0.8
92,90,75,**51**,33,30,29,20	≥ 0.4	1118	0.8		92,90,78,75,64,58,**51**,20,5	≥ 0.1	1119	0.8
92,90,75,**51**,36,33,32,30,29,21,20,16,15,12	≥ 0.3	1116	0.8					
92,90,77,75,**51**,36,34,33,32,31,30,29,26,23,21,20,16,15,12	≥ 0.2	1116	0.8					
Full PES		1116	0.8		Full PES		1116	0.8
C=O stretching (Mode 77; ω=1714 cm^{-1}, I_{HO} = 235.6)								
PES type	q_R	$\upsilon_{C=O}$	$I_{C=O}$		**PES type**	ξ_R	$\upsilon_{C=O}$	$I_{C=O}$
Diagonal		1709	231.8		Diagonal		1709	231.8
77,43,28,23,16,13,10,7,6,5	≥ 0.5	1699	232.3		90,**77**,75,72,70,58,56,45,44,43,20	≥ 0.2	1697	232.0
77,45,43,28,27,26,23,20,16,13,10,7,6,5	≥ 0.4	1699	232.5		90,**77**,75,72,70,65,61,60,58,56,54,50,45,44,43,29,23,22,20,16	≥ 0.1	1696	232.5
77,56,45,43,28,27,26,24,23,22,20,16,15,13,12,10,9,7,6,5,4	≥ 0.3	1700	232.7					
77,75,58,56,45,44,43,37,36,31,29,28,27,26,24,23,22,21,20,16,15,14,13,12,10,9,8,7,6,5,4	≥ 0.2	1697	232.9					
Full PES		1681	233.1		Full PES		1681	233.1

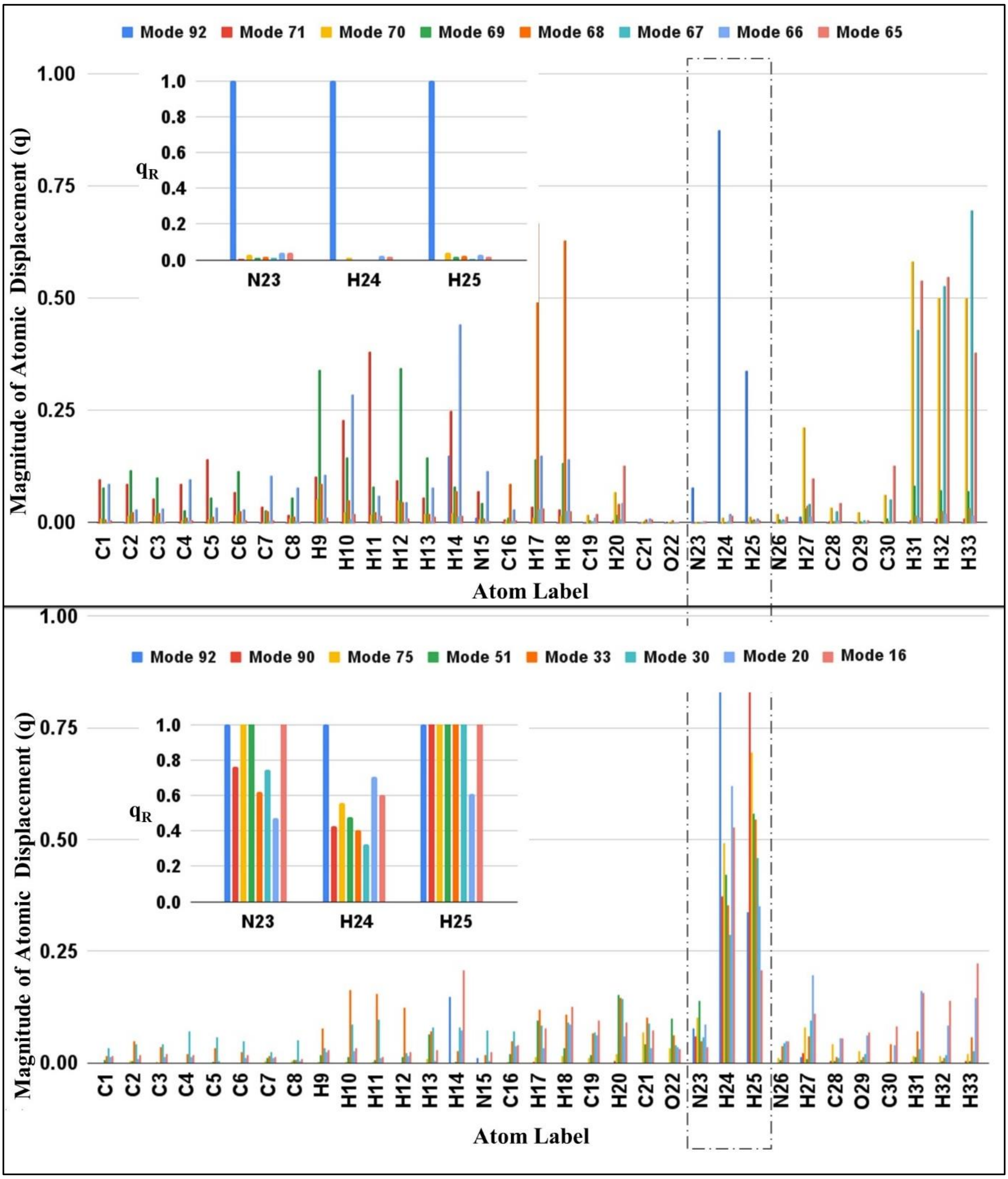

Figure S9a. Normal mode analysis of Anti-symmetric NH_2 stretching (Mode **92**) of NATA. The upper and lower panels represent some weakly and strongly coupled normal modes, respectively, with N-H stretching. Displacements during different modes are given in different colors, where normal mode displacement of H24 atom is taken as reference.

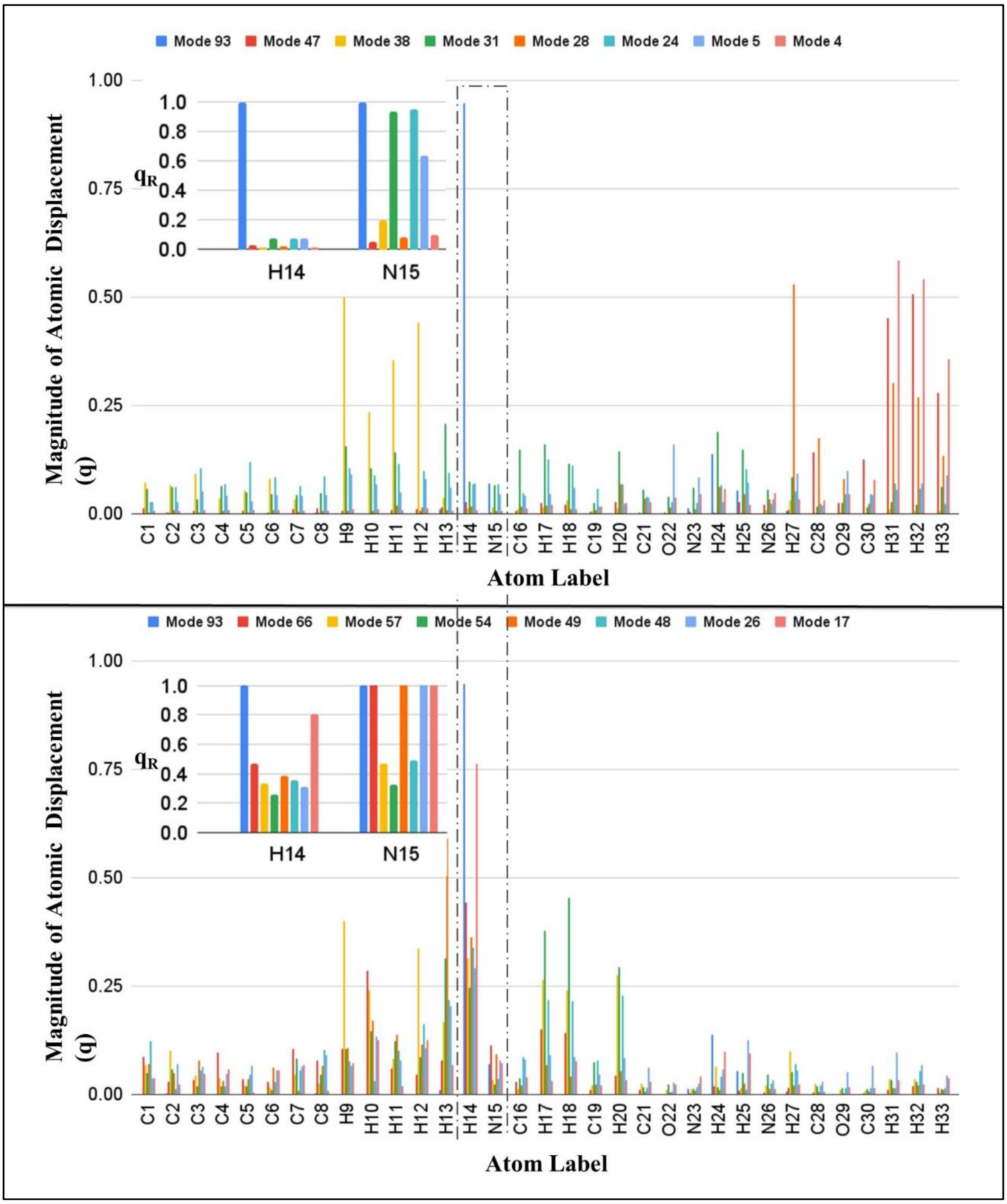

Figure S9b. Normal mode analysis of Indole N-H stretching (Mode **93**) of NATA. The upper and lower panels represent some weakly and strongly coupled normal modes, respectively, with N-H stretching. Displacements during different modes are given in different colors, where normal mode displacement of H14 atom is taken as reference.

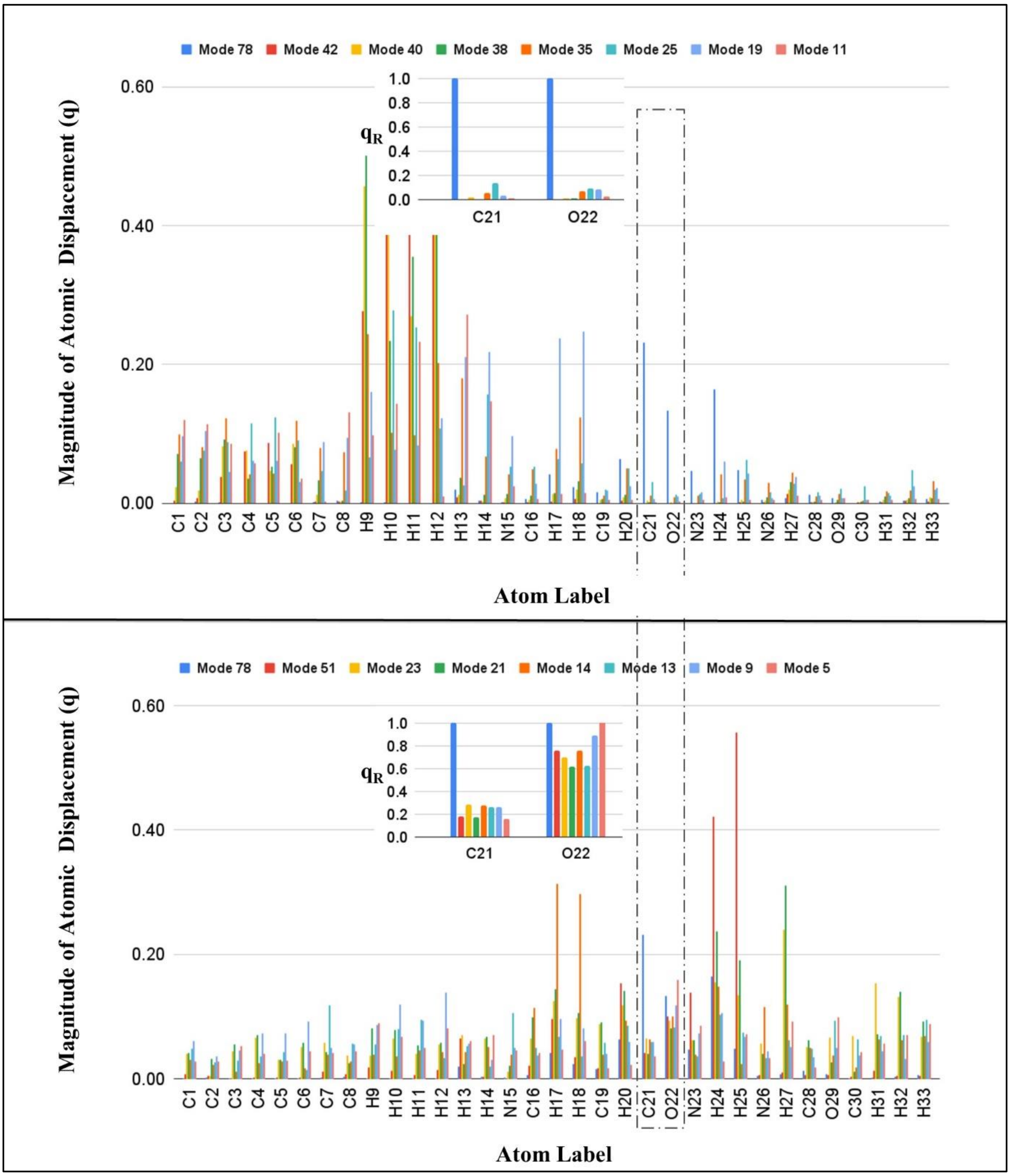

Figure S9c. Normal mode analysis of C=O stretching (Mode **78**) of NATA. The upper and lower panels represent some weakly and strongly coupled normal modes, respectively, with C=O stretching. Displacements during different modes are given in different colors, where normal mode displacement of O22 atom is taken as reference.

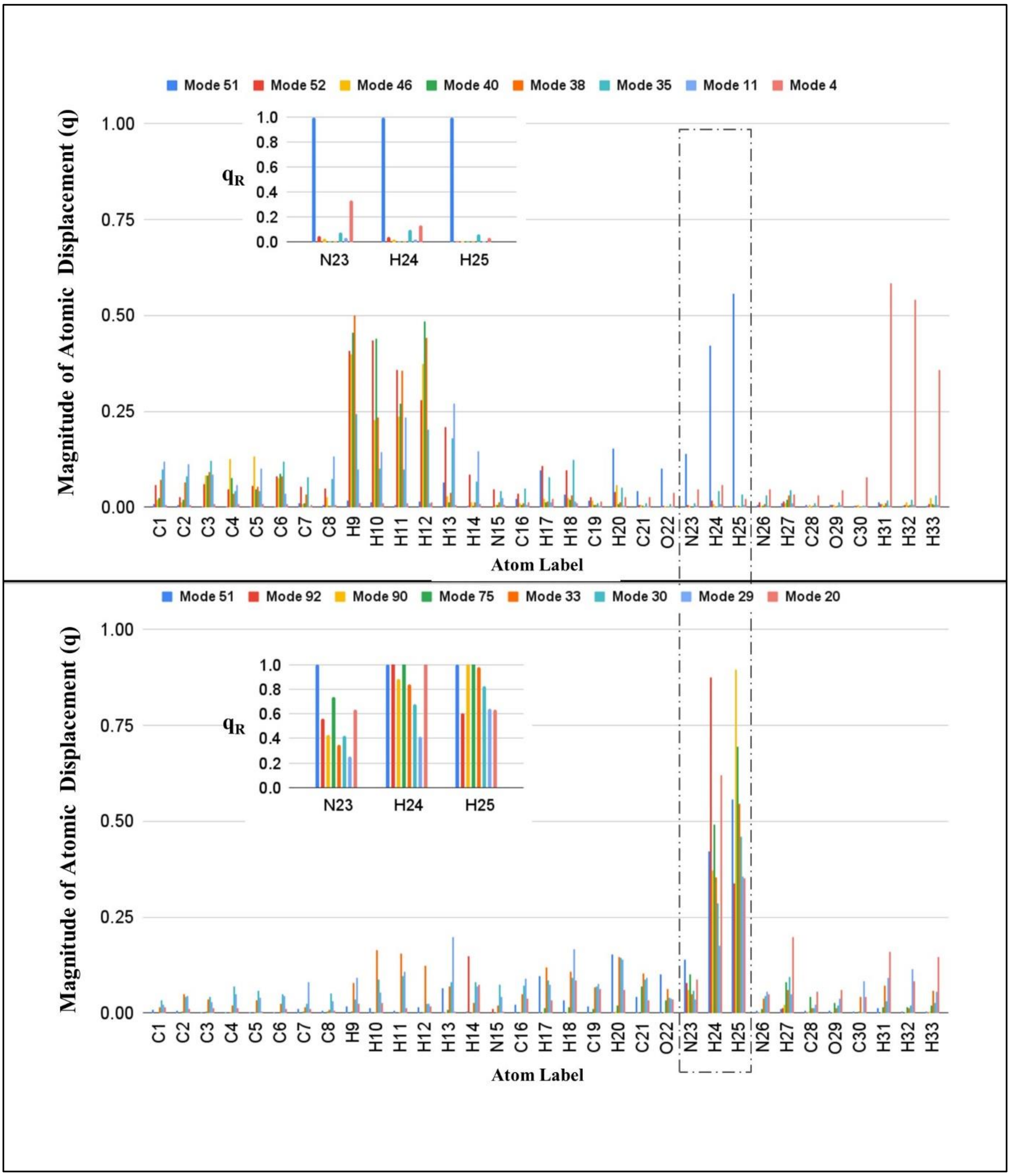

Figure S9d. Normal mode analysis of NH_2 bending (Mode **51**) of NATA. The upper and lower panels represent some weakly and strongly coupled normal modes, respectively, with NH_2 bending. Displacements during different modes are given in different colors, where normal mode displacement of H25 atom is taken as reference.

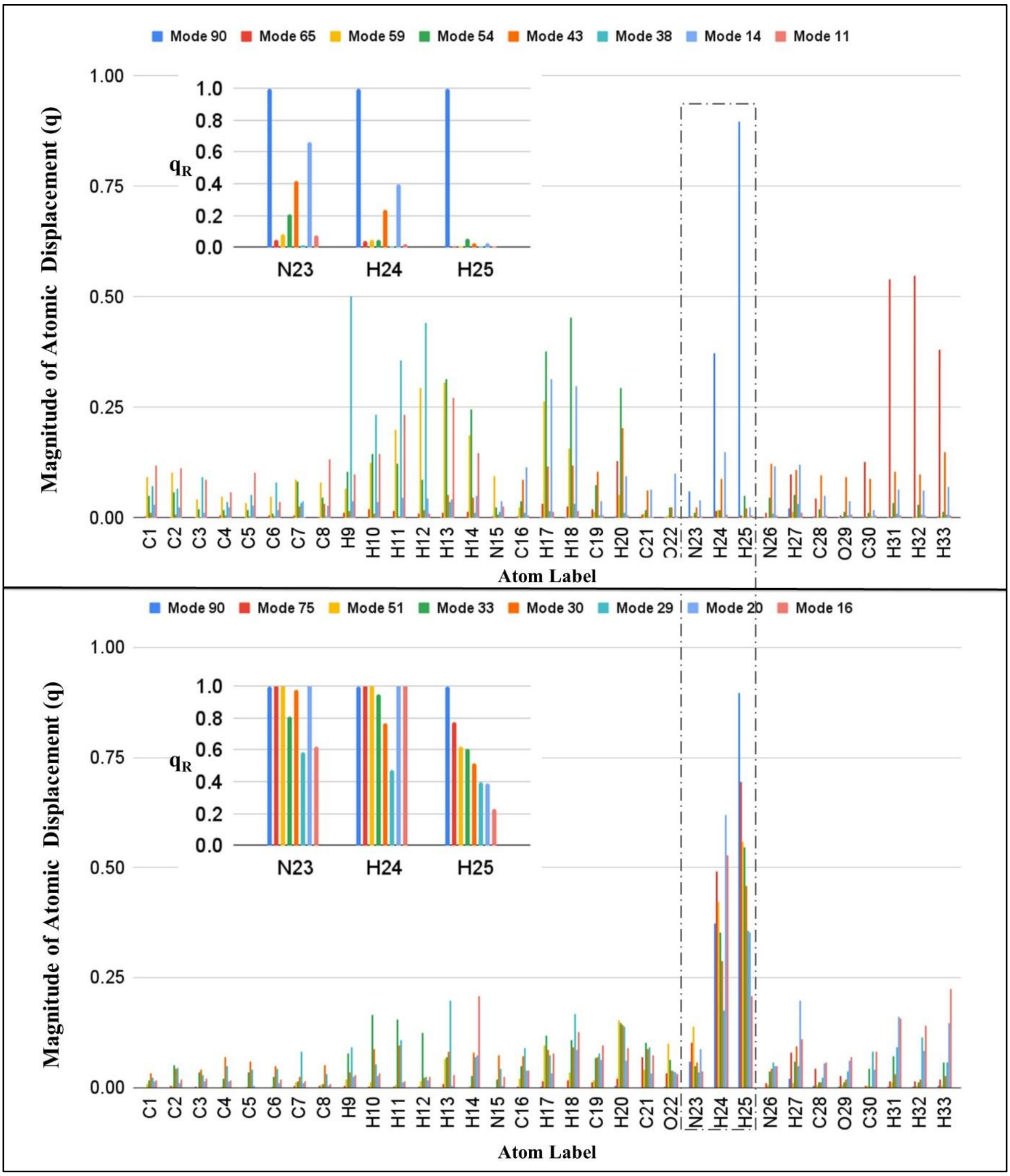

Figure S9e. Normal mode analysis of Symmetric N-H stretching (Mode **90**) of NATA. The upper and lower panels represent some weakly and strongly coupled normal modes, respectively, with N-H stretching. Displacements during different modes are given in different colors, where normal mode displacement of H25 atom is taken as reference.

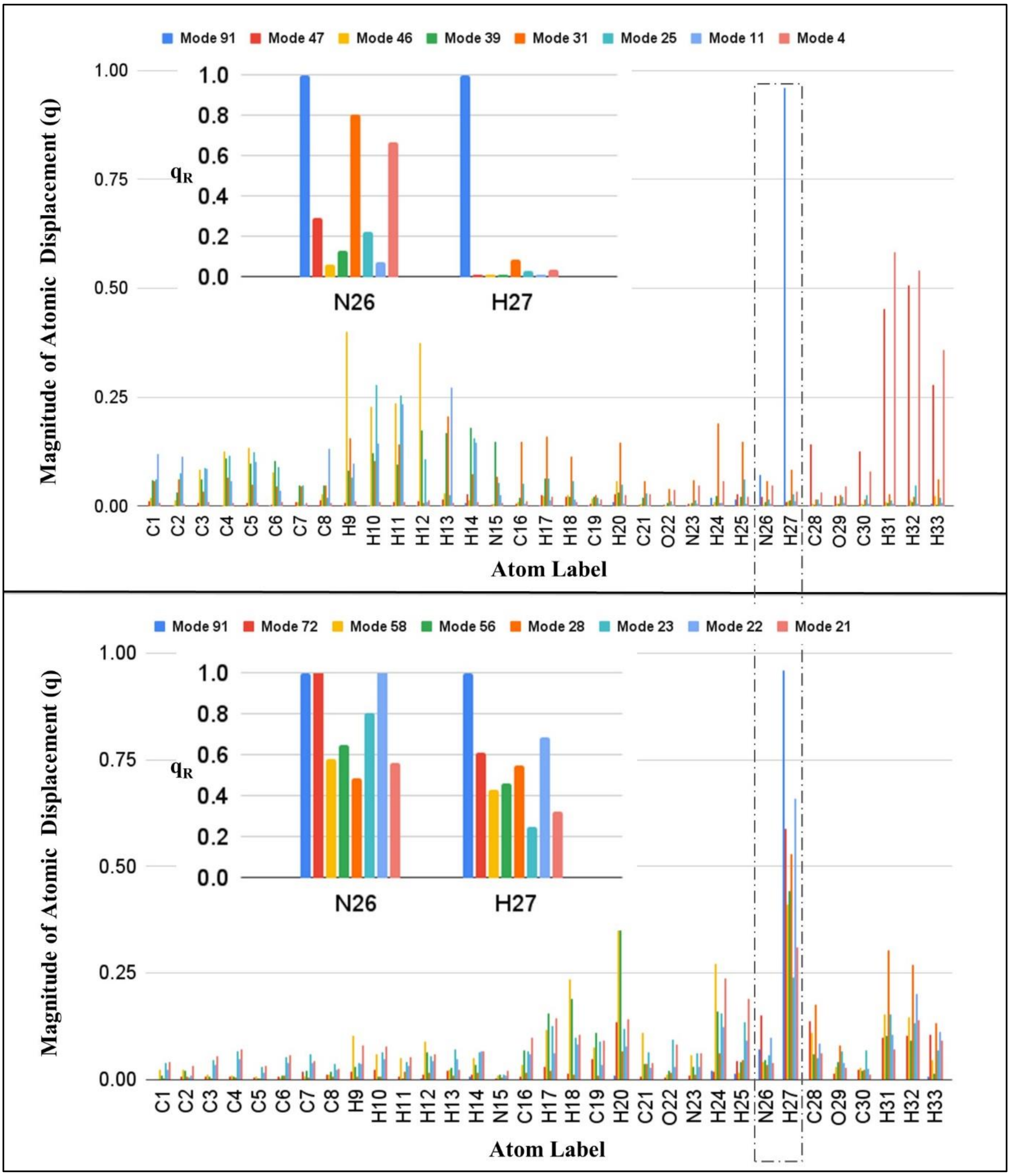

Figure S9f. Normal mode analysis of φ N-H stretching (Mode **91**) of NATA. The upper and lower panels represent some weakly and strongly coupled normal modes, respectively, with φ N-H stretching. Displacements during different modes are given in different colors, where normal mode displacement of H27 atom is taken as reference.