

Understanding Fermi Resonances in the complex vibrational spectra of the methyl groups in methylamines

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Electronic Supplementary Information

The following information contains the random sampling method for conformer structure search, the procedure for calculating Localized Normal Mode (LNM), the Cartesian coordinate of the optimized geometries and the LNM's on methyl groups for the amine molecules/clusters in this study, vibrational spectra of the C-H stretching region of MMA dimer recorded at (a) DICP and (b) IITB, and vibrational spectra of the C-H stretching region of DMA monomer simulated with DoFs on only one and both methyl-groups on DMA monomer.

The random sampling method for conformer structure search

The structures of neutral $(\text{MMA})_n$ and $(\text{DMA})_n$ have been searched previously in previous research^{1,2} using this method, and only brief description is given here. The structures of $(\text{NH}_3)_n$ have been investigated previously for $n = 3-4$, and the stable conformers form hydrogen-bonds (HB) in a cyclic form; based on the structures of $(\text{NH}_3)_n$, we can generate different conformers of $(\text{MMA})_n$, $(\text{DMA})_n$ and $(\text{TMA})_n$ by replacing corresponding amount of hydrogen atom on each ammonia by methyl groups. For $(\text{MMA})_n$ and $(\text{DMA})_n$, only free (non HB) hydrogen atom are replaced by methyl groups. These initial structures were first checked with their structural similarity following the procedure we developed earlier, and only distinct conformers undergo two-step geometry optimizations (first by B3LYP/6-31+G* and then verified by MP2/aug-cc-pVDZ). In all cases in this research, the local minima are located within a few hundred initial guesses.

The procedure for calculating Localized Normal Mode

In many larger molecular systems, the normal modes are delocalized over whole molecule; if we are interested in specific characteristics of a fragment in the system, the interpretation using normal mode analysis becomes extremely complicated; there will be many normal modes contributing to the vibration of that fragment, and we have to include them all to present its vibrational properties, which also makes us to include a large portion of other part of the system. However, in many cases, the IR spectra for these usually show the characteristics of that fragment, indicating that there should be a better way to present the vibrational properties.

A natural answer to the above situation is to constrain the vibrational mode into the target fragment. Many methods are then proposed for this purpose; among the methods, the simplest one is the Partial Hessian vibrational analysis (PHVA)³ proposed by Head, in which they diagonalize the partial Hessian matrix to obtain the vibration for adsorbates on surfaces. This method is one of the simplest way to constrained vibrational mode vectors on to specific region, and many researchers have applied PHVA to different systems.^{4,5}

To differentiate the original normal mode analysis and the projected vibration mode, we use the term “global normal mode” (GNM) for the original normal mode analysis across the whole molecular system; in our study, when we mentioned "localized normal mode" (LNM), we utilize the concept of PHVA: we divide the Hessian into a few sub-matrices of different fragments and then diagonalize them individually, resulting in the LNM as the diagonalizing matrices. We then choose some of the vectors from LNMs, scan the reduced-dimensional PES, and perform anharmonic vibrational analysis using the DVR method. Note that the vector space spanned by LNM coordinates is exactly same as the calculation along GNM if all of the LNMs/GNMs are included. The major difference between the two approaches occurs when we ignore some modes in the reduced-dimensional the vibrational analysis; the choice of LNM or GNM will result in different loss of the information about the exact PES. Clearly, it is non-trivial to determine which method is better in any specific case; nevertheless, as we have found only negligible vibrational coupling between CH₃ and NH₂ groups in neutral MMA¹ and DMA⁶, we believe the current choice of LNMs is good enough in this study, hence we apply the same idea to this work.

Table S1. Cartesian coordinates (in Angstrom) of low-energy conformers of monomer, dimer and trimer of MMA and DMA, and the monomer and dimer of TMA. All molecular geometries are optimized at the MP2/aug-cc-pVDZ level, and the dimers and trimers are shown in Figure 1 in the main text.

MMA₁

C	-0.711238	0.000027	0.018591
H	-1.118714	0.886668	-0.488968
H	-1.118739	-0.886044	-0.489945
H	-1.079037	-0.000539	1.061334
N	0.754345	0.000095	-0.125862
H	1.151620	-0.813678	0.343450
H	1.151591	0.813542	0.344038

MMA_{2a}

N	-2.980786	0.090303	-0.408734
C	-3.442515	-0.464043	0.873658
H	-3.575467	0.874343	-0.676490
H	-2.035656	0.469383	-0.295413
N	0.161491	0.317226	-0.212864
C	0.127277	-1.137888	0.034247
H	0.887950	0.752080	0.355867
H	0.422850	0.495269	-1.183012
H	-3.433848	0.247798	1.720917
H	-2.803105	-1.318293	1.143716
H	-4.468055	-0.847160	0.760124
H	-0.685674	-1.576330	-0.562440
H	-0.104241	-1.310975	1.095544
H	1.066897	-1.666955	-0.204500

MMA_{2b}

N	-2.772298	0.082847	0.376475
H	-3.105734	0.792010	1.029506
C	-3.695676	-0.012428	-0.764781
H	-1.853372	0.396949	0.049810
N	0.296418	0.268488	-0.376439
H	0.368901	-0.548614	-0.983261
C	0.612603	-0.114161	1.014138
H	0.987291	0.934338	-0.722324

H	-3.841955	0.928986	-1.327941
H	-4.680430	-0.355993	-0.412993
H	-3.316241	-0.770578	-1.466629
H	0.564126	0.783692	1.647872
H	1.605405	-0.578879	1.149019
H	-0.157114	-0.814117	1.369191

MMA_{3a}

N	-1.781977	-0.284033	0.713211
H	-2.571749	-0.224470	1.355677
C	-2.272705	-0.291147	-0.675822
H	-1.213079	0.557060	0.869424
N	1.136968	-1.401221	0.713211
C	1.388493	-1.822646	-0.675822
H	0.124112	-1.329089	0.869425
H	1.480274	-2.114964	1.355678
N	0.645008	1.685254	0.713211
H	1.091474	2.339436	1.355678
C	0.884213	2.113793	-0.675822
H	1.088968	0.772028	0.869425
H	-2.841901	0.610033	-0.969924
H	-2.915249	-1.170123	-0.835403
H	-1.413509	-0.385636	-1.357319
H	1.040722	-1.031317	-1.357319
H	0.892647	-2.766175	-0.969923
H	2.470981	-1.939616	-0.835404
H	1.949256	2.156142	-0.969923
H	0.444268	3.109740	-0.835404
H	0.372787	1.416950	-1.357320

MMA_{3b}

N	1.702852	0.037583	-0.760684
H	2.187823	0.312815	-1.614256
H	1.216377	0.867686	-0.403361
N	-0.707940	-1.445100	0.508601
H	-0.403304	-2.249950	1.056214
H	0.074295	-1.200870	-0.111167
N	-0.438281	1.661748	0.726310
H	-0.648427	2.272387	1.515403

H	-0.628007	0.699947	1.031240
C	2.678941	-0.401162	0.252352
H	2.136597	-0.642730	1.179499
H	3.183146	-1.317277	-0.091503
H	3.453260	0.347169	0.501124
C	-1.326479	1.981199	-0.405147
H	-1.154561	3.019526	-0.726883
H	-1.069912	1.324852	-1.251307
H	-2.405260	1.859328	-0.195064
C	-1.885427	-1.813344	-0.296653
H	-2.723115	-2.067211	0.370477
H	-2.192414	-0.943410	-0.896398
H	-1.725126	-2.662033	-0.986919

DMA₁

C	1.386965	0.000000	-0.471959
H	1.390171	0.107885	-1.568361
H	1.924790	0.859464	-0.045202
H	1.942491	-0.928033	-0.220142
C	-0.723689	-1.183193	-0.471959
H	-0.817397	-1.129636	-1.568361
H	-1.737507	-1.193551	-0.045202
H	-0.221864	-2.141329	-0.220142
N	0.000000	0.000000	0.000000
H	0.000000	0.000000	1.020182

DMA_{2a}

N	0.000000	-0.000000	0.000000
H	-0.000000	-0.000000	1.025903
N	0.895353	0.000000	2.919109
H	0.562921	0.000000	3.883437
C	-0.680586	1.206886	-0.468563
H	-0.196618	2.096453	-0.036658
H	-0.597668	1.274221	-1.566047
H	-1.761290	1.235978	-0.209768
C	1.692752	1.210656	2.684120
H	1.960820	1.248765	1.616361
H	1.094115	2.101979	2.924597
H	2.629631	1.240858	3.276763

C	-0.680586	-1.206886	-0.468563
H	-0.196618	-2.096453	-0.036658
H	-0.597668	-1.274221	-1.566047
H	-1.761290	-1.235978	-0.209768
C	1.692752	-1.210656	2.684120
H	1.960820	-1.248765	1.616361
H	1.094115	-2.101979	2.924597
H	2.629631	-1.240858	3.276763

DMA_{2b}

N	1.303344	0.527357	0.138586
H	0.435803	0.007640	-0.034446
N	-1.572556	-0.663961	-0.103357
C	2.436495	-0.346424	-0.164593
H	2.356269	-0.710964	-1.199792
H	3.376045	0.224190	-0.077357
H	2.512262	-1.225446	0.512602
C	-2.132336	0.642250	-0.471776
H	-1.652236	1.420045	0.142955
H	-1.904338	0.858750	-1.525442
H	-3.228547	0.709473	-0.318624
C	1.322786	0.943315	1.540329
H	2.213296	1.566020	1.727669
H	0.434428	1.555509	1.761362
H	1.351292	0.093167	2.257494
C	-1.922700	-1.028850	1.274018
H	-1.538034	-2.034065	1.501218
H	-1.442739	-0.315564	1.962692
H	-3.013973	-1.011397	1.471443
H	-1.938913	-1.373166	-0.738416

DMA_{3a}

N	-0.461447	-1.717105	-0.148076
H	0.432336	-1.215383	-0.240059
N	-1.256548	1.258011	-0.147347
H	-1.269075	0.233024	-0.238328
N	1.717527	0.459031	-0.150437
H	0.835986	0.982287	-0.240560
C	-0.539422	-2.282203	1.200660

H	-0.413926	-1.482174	1.946371
H	-1.532094	-2.736982	1.353691
H	0.225046	-3.063537	1.395500
C	2.659511	0.921827	-1.171205
H	3.565318	0.293670	-1.149135
H	2.201849	0.826104	-2.167372
H	2.975826	1.976822	-1.030019
C	-2.129971	1.843267	-1.166214
H	-2.038841	2.941779	-1.143349
H	-1.819841	1.495636	-2.163178
H	-3.201553	1.589583	-1.023525
C	-0.533215	-2.765271	-1.167723
H	-1.530082	-3.235624	-1.143664
H	-0.388817	-2.322025	-2.164541
H	0.222498	-3.566568	-1.026926
C	2.248070	0.672903	1.197631
H	1.493675	0.380938	1.944307
H	3.138500	0.040483	1.348694
H	2.542805	1.725454	1.392893
C	-1.704874	1.609383	1.201743
H	-1.073628	1.101403	1.946973
H	-1.602156	2.696598	1.353573
H	-2.763462	1.338186	1.398473

DMA_{3b}

N	2.172190	-0.893209	-0.036388
N	0.348077	1.539114	-0.128974
C	1.640639	-1.634210	-1.190591
C	1.654371	-1.453232	1.221948
H	2.046538	-1.211613	-2.122201
H	2.071488	-0.896932	2.075120
H	1.876710	-2.717023	-1.158836
H	0.545273	-1.525985	-1.192134
H	1.892130	-2.528662	1.349148
H	0.558297	-1.347522	1.218560
H	3.190547	-0.961678	-0.037011
C	0.331948	2.150449	1.201503
C	0.545422	2.542386	-1.175840
H	0.260167	1.363886	1.968307

H	0.627470	2.044799	-2.154120
H	1.232378	2.764437	1.414643
H	-0.551158	2.803902	1.298199
H	1.451380	3.166119	-1.022057
H	-0.325329	3.218195	-1.208797
H	1.117581	0.855993	-0.161815
N	-1.685857	-0.750264	0.012620
H	-1.106784	0.090287	-0.123760
C	-2.526530	-0.935044	-1.169630
H	-3.081161	-1.884834	-1.086806
H	-1.894390	-0.988933	-2.069820
H	-3.270775	-0.122177	-1.315968
C	-2.499861	-0.560419	1.212663
H	-3.064121	-1.483115	1.429022
H	-1.847545	-0.352749	2.075330
H	-3.234067	0.269761	1.124257

TMA₁

N	0.000002	0.000001	0.411684
C	-0.938296	1.013653	-0.066587
H	-1.948584	0.790148	0.309143
H	-0.637564	2.003704	0.309134
H	-0.979272	1.057910	-1.179538
C	1.346998	0.305762	-0.066593
H	1.658580	1.292453	0.309126
H	2.054043	-0.449701	0.309135
H	1.405811	0.319107	-1.179544
C	-0.408701	-1.319415	-0.066583
H	0.290009	-2.082596	0.309139
H	-1.416472	-1.554000	0.309150
H	-0.426554	-1.377028	-1.179534

TMA₂

N	1.652571	-0.194606	0.243066
N	-1.658027	0.235094	-0.266373
C	1.411068	-1.406752	-0.540185
H	1.322205	-2.273577	0.133772
H	0.471132	-1.290350	-1.099348
H	2.236858	-1.608571	-1.260460

C	2.897170	-0.327663	0.998593
H	3.068280	0.582209	1.594873
H	2.824979	-1.186404	1.684194
H	3.779102	-0.482504	0.334924
C	1.735869	0.954154	-0.659440
H	0.791818	1.040520	-1.217115
H	1.892941	1.875121	-0.075789
H	2.575639	0.853821	-1.384821
C	-1.416551	1.447241	0.516887
H	-0.476663	1.330832	1.076130
H	-1.327619	2.314060	-0.157070
H	-2.242392	1.649085	1.237097
C	-2.902620	0.368151	-1.021912
H	-3.784558	0.522980	-0.358249
H	-2.830427	1.226901	-1.707502
H	-3.073718	-0.541715	-1.618205
C	-1.741334	-0.913667	0.636131
H	-1.898374	-1.834637	0.052474
H	-0.797292	-1.000021	1.193823
H	-2.581121	-0.813347	1.361493

Table S2. Harmonic frequencies (in cm^{-1}) of the selected 6 Localized Normal Modes of MMA monomer/trimer, DMA monomer/trimer and TMA monomer/dimer. The LNMs are obtained using PHVA^{3,4} on the hessian matrices calculated at the level of MP2/aug-cc-pVDZ. The naming scheme is based on the notation used for MMA.⁷

	ν_6	ν_5	ν_{12}	ν_3	ν_2	ν_{11}
	$\text{CH}_3^{\text{a}'}\text{s-deform}$	$\text{CH}_3^{\text{a}'}\text{d-deform}$	$\text{CH}_3^{\text{a}''}\text{d-deform}$	$\text{CH}_3^{\text{a}'}\text{d-str}$	$\text{CH}_3^{\text{a}'}\text{d-str}$	$\text{CH}_3^{\text{a}''}\text{d-str}$
MMA_1	1444	1493	1508	3038	3130	3170
$\text{MMA}_{3\text{a}}$	1439	1492	1508	3033	3118	3155
DMA_1	1437	1481	1498	2992	3109	3163
$\text{DMA}_{3\text{a}}$	1432	1479	1499	2989	3094	3145
TMA_1	1432	1479	1485	2953	3106	3160
TMA_2	1426	1482	1490	2954	3100	3159

Table S3. Sub-matrices (in cm^{-1}) of the quantum states involved in Fermi resonance under FBR. The off-diagonal terms illustrate the coupling strength between two quantum states and the diagonal terms stands for the peak positions of both the stretching fundamental and overtones of umbrella/bending modes as shown in **Figure 5**.

MMA ₁	v ₃	v ₂	v ₁₁	2v ₆	v ₆ +v ₅	v ₆ +v ₁₂	2v ₅	v ₅ +v ₁₂	2v ₁₂
v ₃	2869.7	-3.8	0.0	-31.7	-15.0	0.0	-14.1	0.0	22.3
v ₂	-3.8	2936.9	0.0	30.3	-8.3	0.0	21.3	0.0	-1.1
v ₁₁	0.0	0.0	2967.0	0.0	0.0	8.4	0.0	-25.0	0.0
2v ₆	-31.7	30.3	0.0	2856.6	3.1	0.0	0.4	0.0	-0.3
v ₆ +v ₅	-15.0	-8.3	0.0	3.1	2882.5	0.0	2.9	0.0	-0.3
v ₆ +v ₁₂	0.0	0.0	8.4	0.0	0.0	2894.2	0.0	-2.6	0.0
2v ₅	-14.1	21.3	0.0	0.4	2.9	0.0	2909.5	0.0	-0.4
v ₅ +v ₁₂	0.0	0.0	-25.0	0.0	0.0	-2.6	0.0	2926.0	0.0
2v ₁₂	22.3	-1.1	0.0	-0.3	-0.3	0.0	-0.4	0.0	2937.5

DMA ₁	v ₃	v ₂	v ₁₁	2v ₆	v ₆ +v ₅	v ₆ +v ₁₂	2v ₅	v ₅ +v ₁₂	2v ₁₂
v ₃	2827.8	4.3	1.4	-29.0	-12.6	5.8	-11.1	6.3	19.0
v ₂	4.3	2925.8	1.3	-31.7	8.9	2.6	-18.4	-11.8	9.5
v ₁₁	1.4	1.3	2968.0	-10.3	-2.3	-8.3	-16.6	15.4	-10.1
2v ₆	-29.0	-31.7	-10.3	2850.1	1.7	-1.5	0.4	0.0	-0.3
v ₆ +v ₅	-12.6	8.9	-2.3	1.7	2868.9	-0.5	1.6	0.6	-0.1
v ₆ +v ₁₂	5.8	2.6	-8.3	-1.5	-0.5	2884.5	0.2	-1.4	1.8
2v ₅	-11.1	-18.4	-16.6	0.4	1.6	0.2	2890.5	0.3	-0.3
v ₅ +v ₁₂	6.3	-11.8	15.4	0.0	0.6	-1.4	0.3	2908.1	-0.6
2v ₁₂	19.0	9.5	-10.1	-0.3	-0.1	1.8	-0.3	-0.6	2924.9

TMA ₁	v ₃	v ₂	v ₁₁	2v ₆	v ₆ +v ₅	v ₆ +v ₁₂	2v ₅	v ₅ +v ₁₂	2v ₁₂
v ₃	2793.3	-4.9	0.0	-29.8	6.9	0.0	-7.3	0.0	18.5
v ₂	-4.9	2932.2	0.0	32.9	10.1	0.0	27.5	0.0	-3.9
v ₁₁	0.0	0.0	2966.6	0.0	0.0	14.6	0.0	23.3	0.0
2v ₆	-29.8	32.9	0.0	2850.7	0.3	0.0	0.5	0.0	-0.4
v ₆ +v ₅	6.9	10.1	0.0	0.3	2869.5	0.0	0.5	0.0	0.4
v ₆ +v ₁₂	0.0	0.0	14.6	0.0	0.0	2874.6	0.0	0.4	0.0
2v ₅	-7.3	27.5	0.0	0.5	0.5	0.0	2892.6	0.0	-0.2
v ₅ +v ₁₂	0.0	0.0	23.3	0.0	0.0	0.4	0.0	2899.2	0.0
2v ₁₂	18.5	-3.9	0.0	-0.4	0.4	0.0	-0.2	0.0	2902.7

Figure S1. Comparison of the MMA dimer spectra recorded at (a) DICP and (b) IITB.

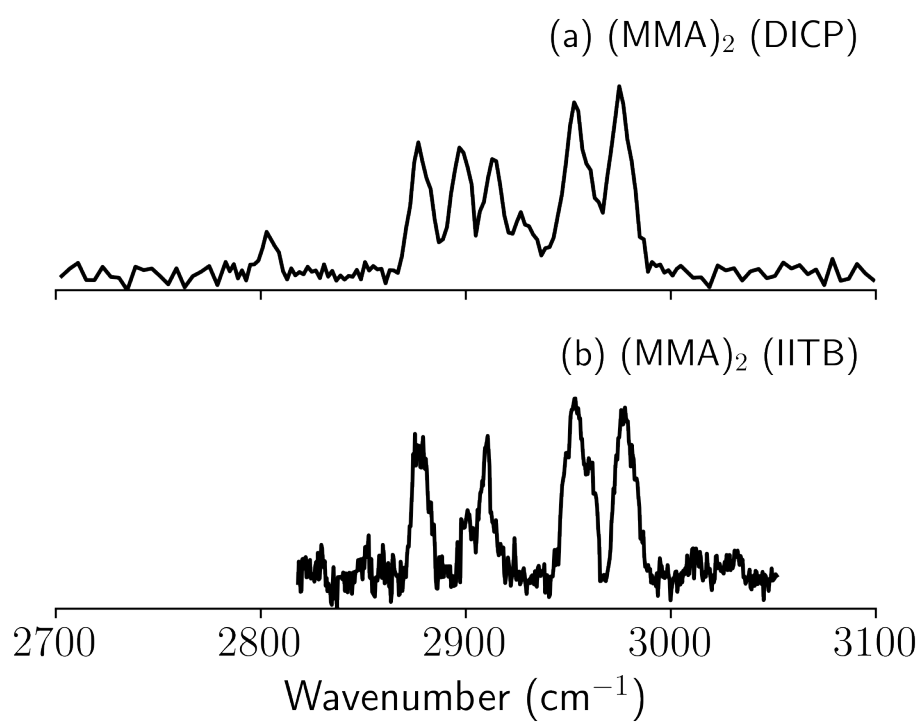


Figure S2. Vibrational Spectra of the C-H stretching region of DMA monomer simulated with (a) six DoFs on one methyl-group and (b) twelve DoFs on both methyl-groups. The similarity between the two spectra evidences that the coupling between the DoFs on the two methyl-groups is weak.

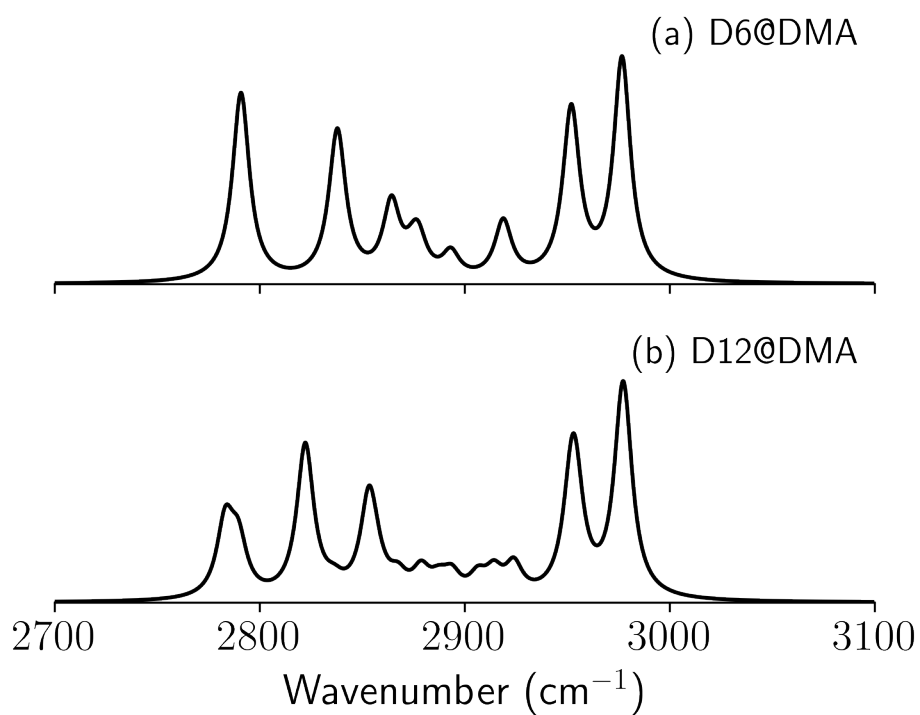


Figure S3. Simulated IR absorption spectra of the methyl groups of (a) MMA, (b) DMA, and (c) TMA monomers simulated with the *ab initio* anharmonic algorithms at the different computation levels. The blue traces represent the result calculated at the level of CCSD/aug-cc-pVDZ, and the green lines represent the calculation at the level of CCSD(T)-F12/aug-cc-pVTZ. The experimental spectra are shown as grey traces for the sake of comparison. We can see that the raising of the computational level only changes the positions of the peaks slightly; instead, it has more impact on the intensities of the peaks. Calculation on the clusters will certainly take much more computational efforts. To make the computation level in the whole article consistent, we decided to present the comparison at the level of CCSD/aug-cc-pVDZ.

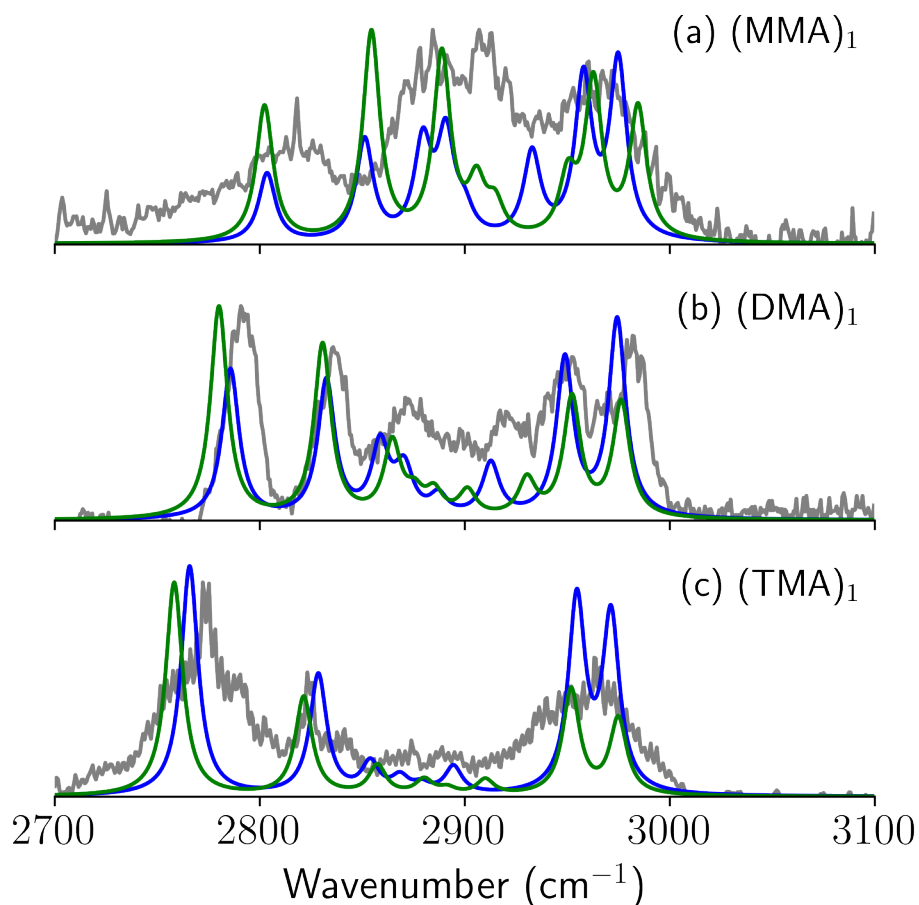
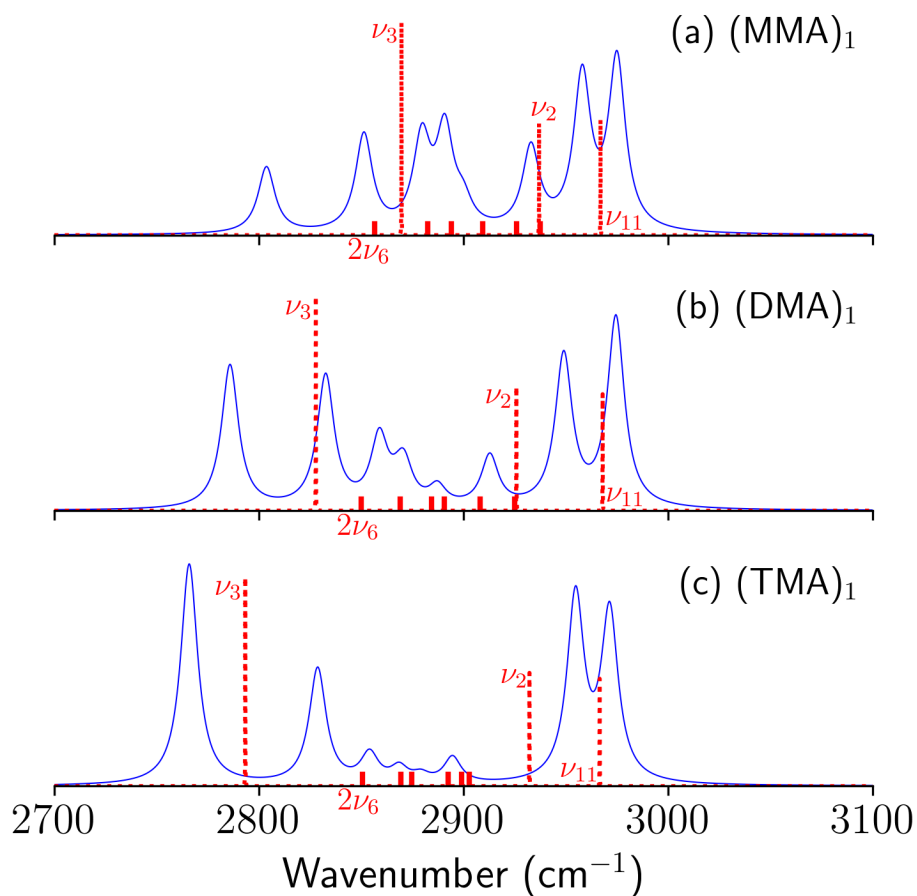


Figure S4. Comparison between the simulated IR absorption spectra (blue traces) of the methyl groups of (a) MMA, (b) DMA and (c) TMA monomers and the positions of three C–H stretching fundamental (red dotted line) and six overtone states of umbrella/bending (red solid sticks) evaluated with the FBR method. The three stretching fundamentals (ν_3 , ν_2 , ν_{11}) and the overtone of umbrella modes ($2\nu_6$) are labelled for convenience.



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