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Supplementary Materials

Spectra–Structure Correlations in Isotopomers of Ethanol (CX_3CX_2OX; X = H, D): Combined Near-Infrared and Anharmonic Computational Study

Krzysztof B. Beć [1,2,*], Justyna Grabska [1], Christian W. Huck [1], and Mirosław A. Czarnecki [2]

[1] Institute of Analytical Chemistry and Radiochemistry, Leopold-Franzens University, Innrain 80/82, CCB-Center for Chemistry and Biomedicine, 6020-Innsbruck, Austria; Justyna.Grabska@ uibk.ac.at (J.G.); Christian.W.Huck@uibk.ac.at (C.W.H.)

[2] Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland; miroslaw.czarnecki@chem.uni.wroc.pl

* Correspondence: Krzysztof.Bec@uibk.ac.at; Tel.: +43-512-507-5783

I. Figures

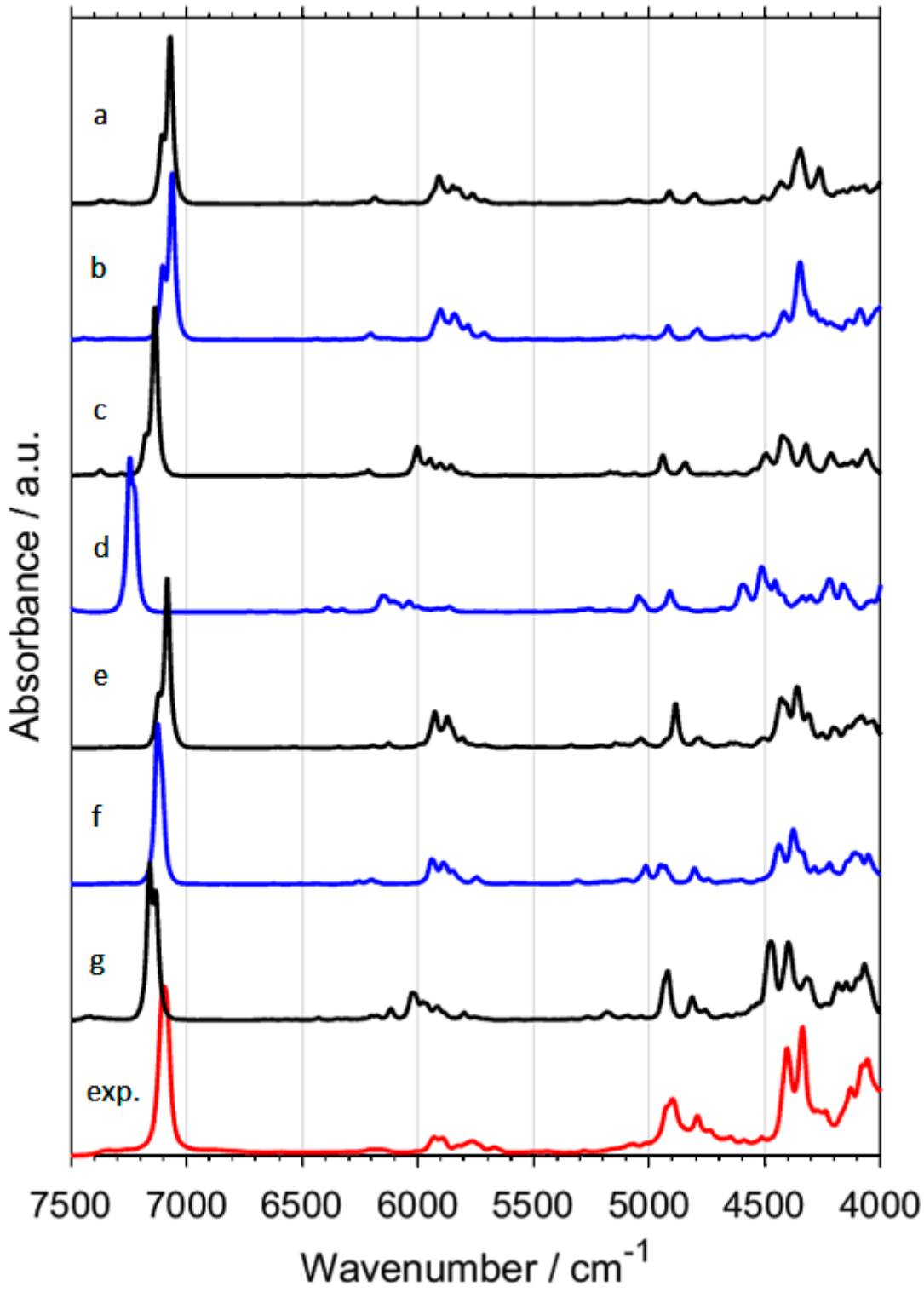

Figure S1. **NIR spectra of CH_3CD_2OH calculated with GVPT2 method at different levels of electronic theory; (a) B3LYP-GD3BJ /6-31G(d,p); (b) B3LYP-GD3BJ /6-31G(d,p)//CPCM; (c) B2PLYP-GD3BJ/6-31G(d,p)//CPCM; (d) MP2/6-31G(d,p)//CPCM; (e) B3LYP-GD3BJ/SNST//CPCM; (f) B2PLYP-GD3BJ/def2-TZVP//CPCM; (g) MP2/aug-cc-pVTZ//CPCM. Experimental spectrum (exp.) of CH_3CD_2OH in CCl_4 (0.1 M).**

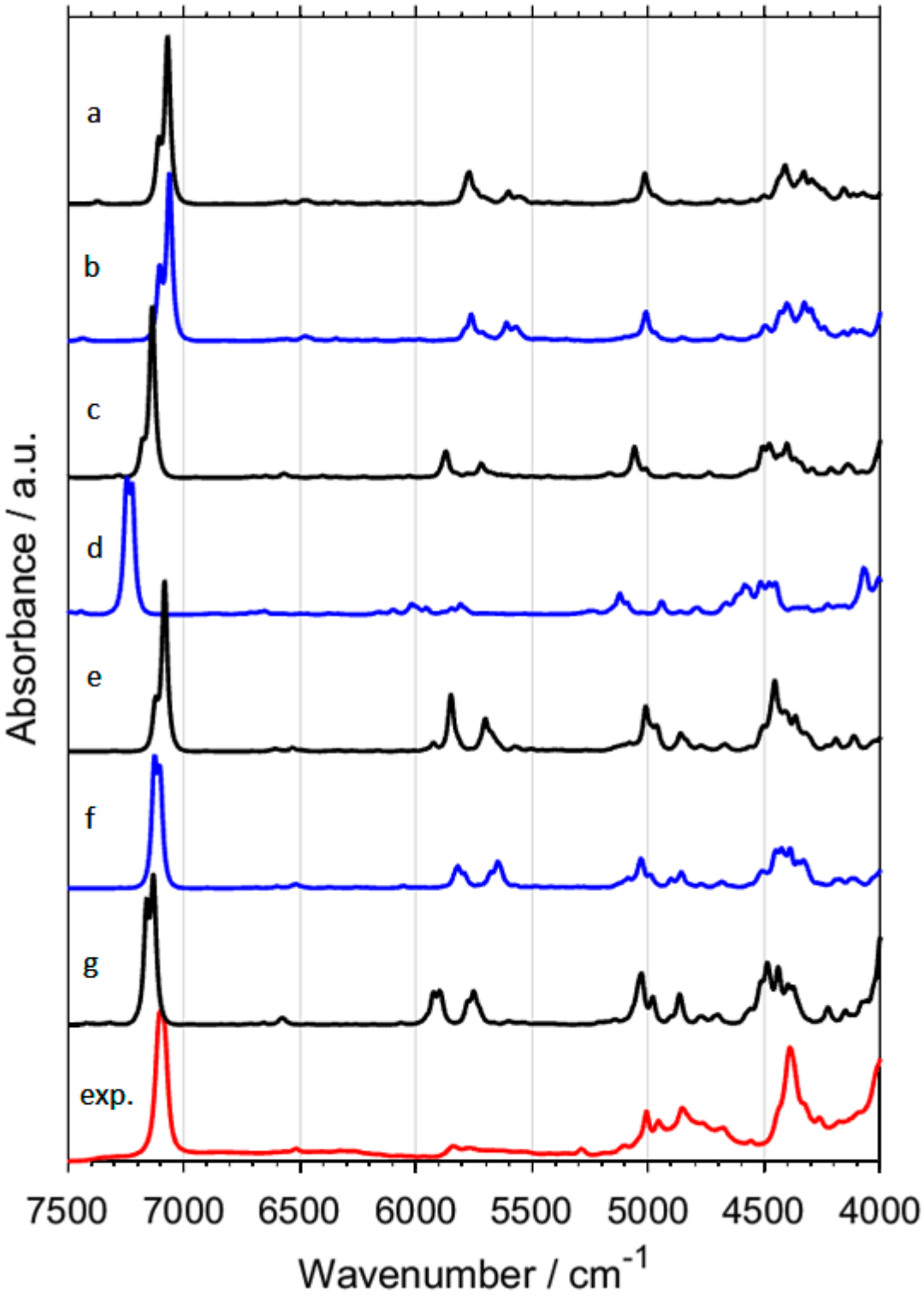

Figure S2. **NIR spectra of CD_3CH_2OH calculated with GVPT2 method at different levels of electronic theory; (a) B3LYP-GD3BJ /6-31G(d,p); (b) B3LYP-GD3BJ /6-31G(d,p)//CPCM; (c) B2PLYP-GD3BJ/6-31G(d,p)//CPCM; (d) MP2/6-31G(d,p)//CPCM; (e) B3LYP-GD3BJ/SNST//CPCM; (f) B2PLYP-GD3BJ/def2-TZVP//CPCM; (g) MP2/aug-cc-pVTZ//CPCM. Experimental spectrum (exp.) of CD_3CH_2OH in CCl_4 (0.1 M).**

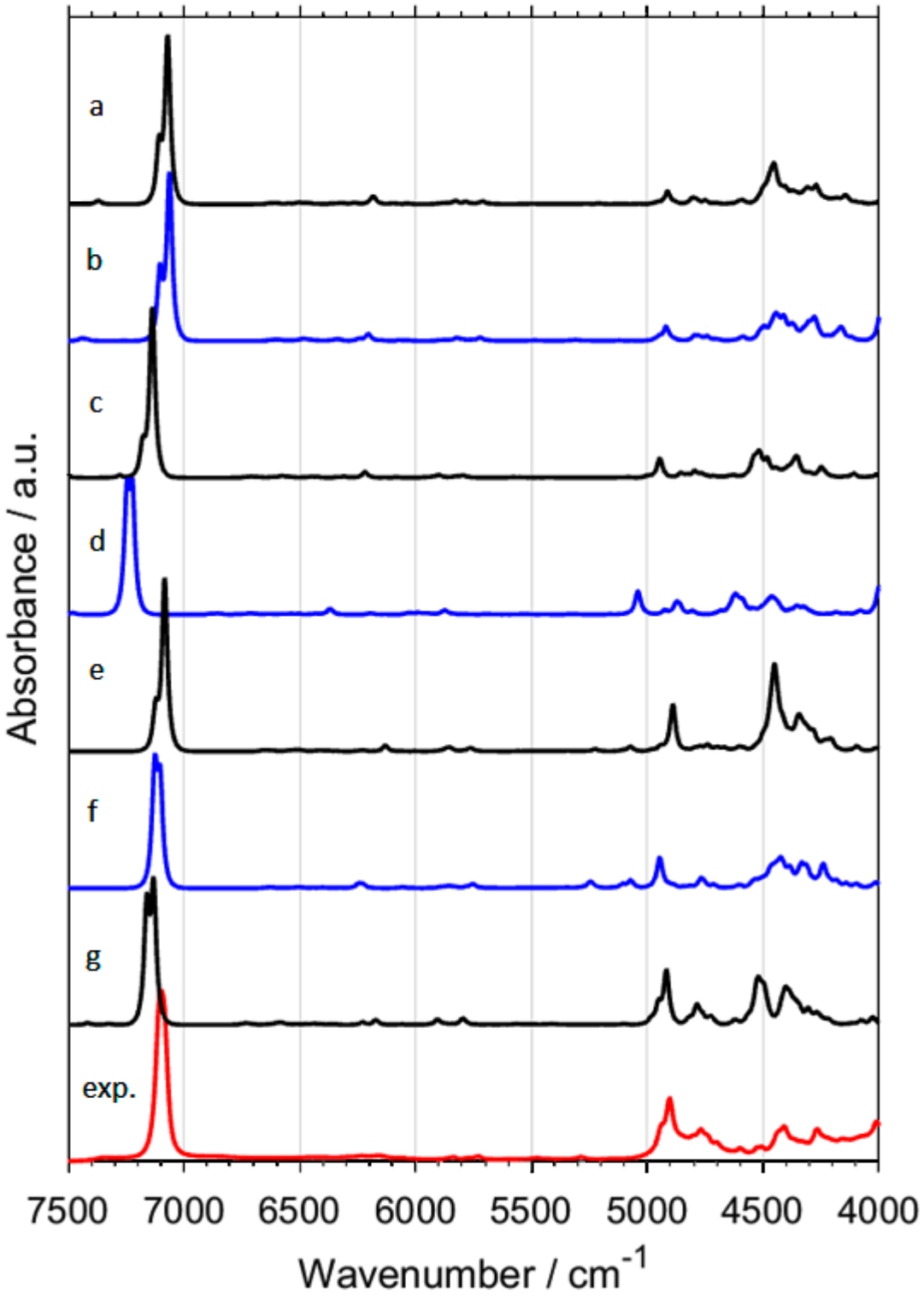

Figure S3. NIR spectra of CD_3CD_2OH calculated with GVPT2 method at different levels of electronic theory; (a) B3LYP-GD3BJ /6-31G(d,p); (b) B3LYP-GD3BJ /6-31G(d,p)//CPCM; (c) B2PLYP-GD3BJ/6-31G(d,p)//CPCM; (d) MP2/6-31G(d,p)//CPCM; (e) B3LYP-GD3BJ/SNST//CPCM; (f) B2PLYP-GD3BJ/def2-TZVP//CPCM; (g) MP2/aug-cc-pVTZ//CPCM. Experimental spectrum (exp.) of CD_3CD_2OH in CCl_4 (0.1 M).

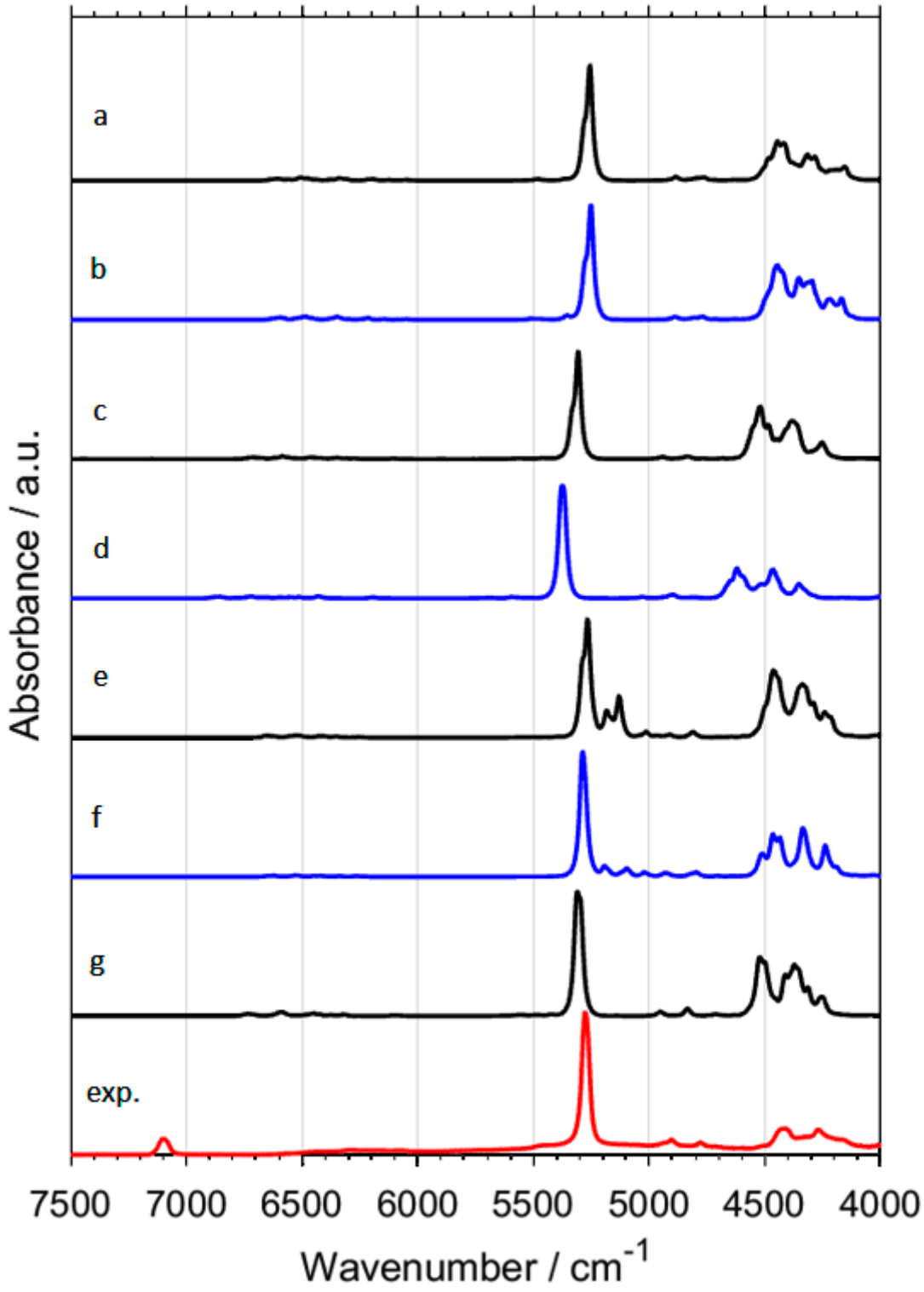

Figure S4. NIR spectra of CD_3CD_2OD calculated with GVPT2 method at different levels of electronic theory; (a) B3LYP-GD3BJ /6-31G(d,p); (b) B3LYP-GD3BJ /6-31G(d,p)//CPCM; (c) B2PLYP-GD3BJ/6-31G(d,p)//CPCM; (d) MP2/6-31G(d,p)//CPCM; (e) B3LYP-GD3BJ/SNST//CPCM; (f) B2PLYP-GD3BJ/def2-TZVP//CPCM; (g) MP2/aug-cc-pVTZ//CPCM. Experimental spectrum (exp.) of CD_3CD_2OD in CCl_4 (0.1 M).

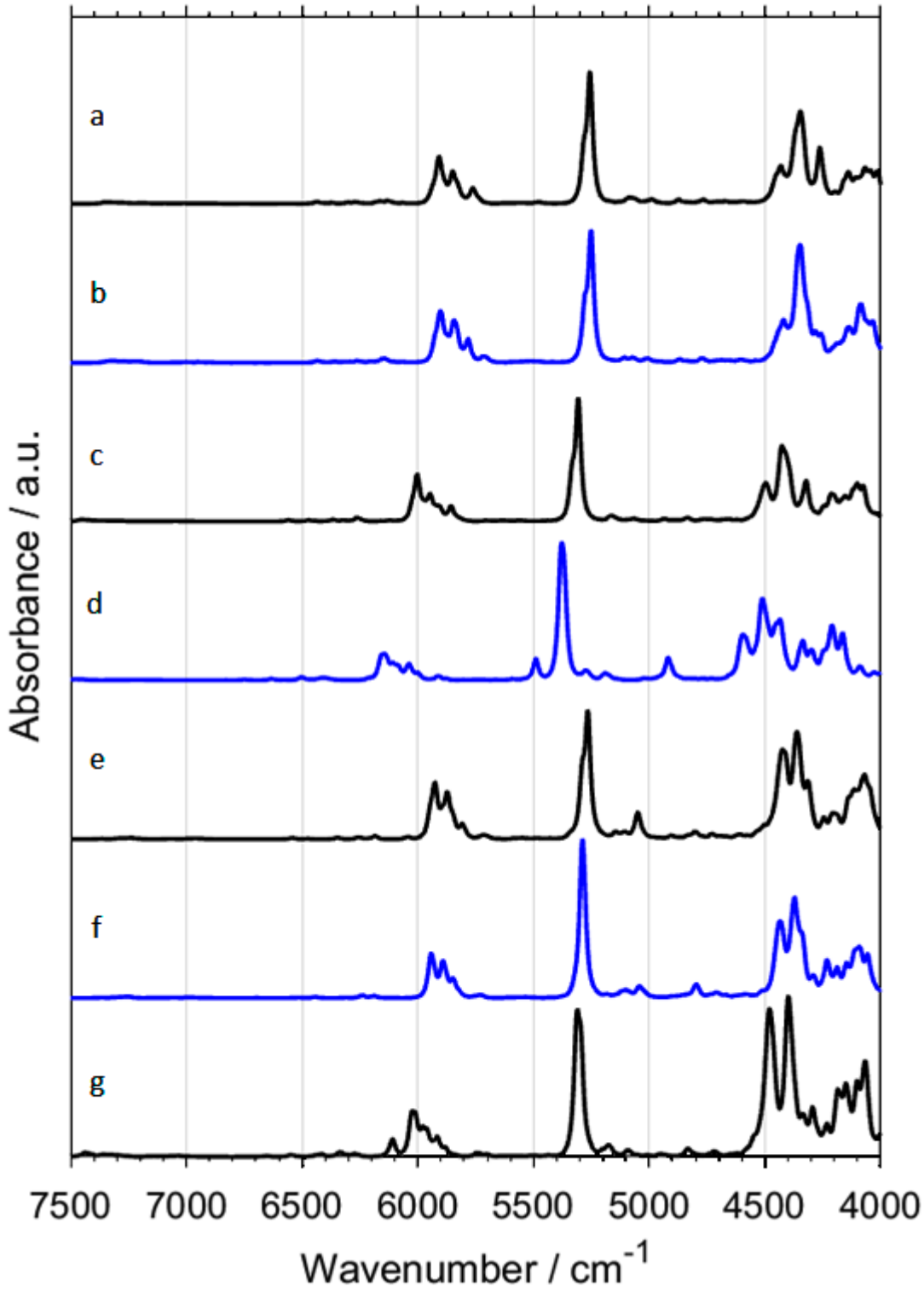

Figure S5. **NIR spectra of CH_3CD_2OD calculated with GVPT2 method at different levels of electronic theory; (a) B3LYP-GD3BJ /6-31G(d,p); (b) B3LYP-GD3BJ /6-31G(d,p)//CPCM; (c) B2PLYP-GD3BJ/6-31G(d,p)//CPCM; (d) MP2/6-31G(d,p)//CPCM; (e) B3LYP-GD3BJ/SNST//CPCM; (f) B2PLYP-GD3BJ/def2-TZVP//CPCM; (g) MP2/aug-cc-pVTZ//CPCM.**

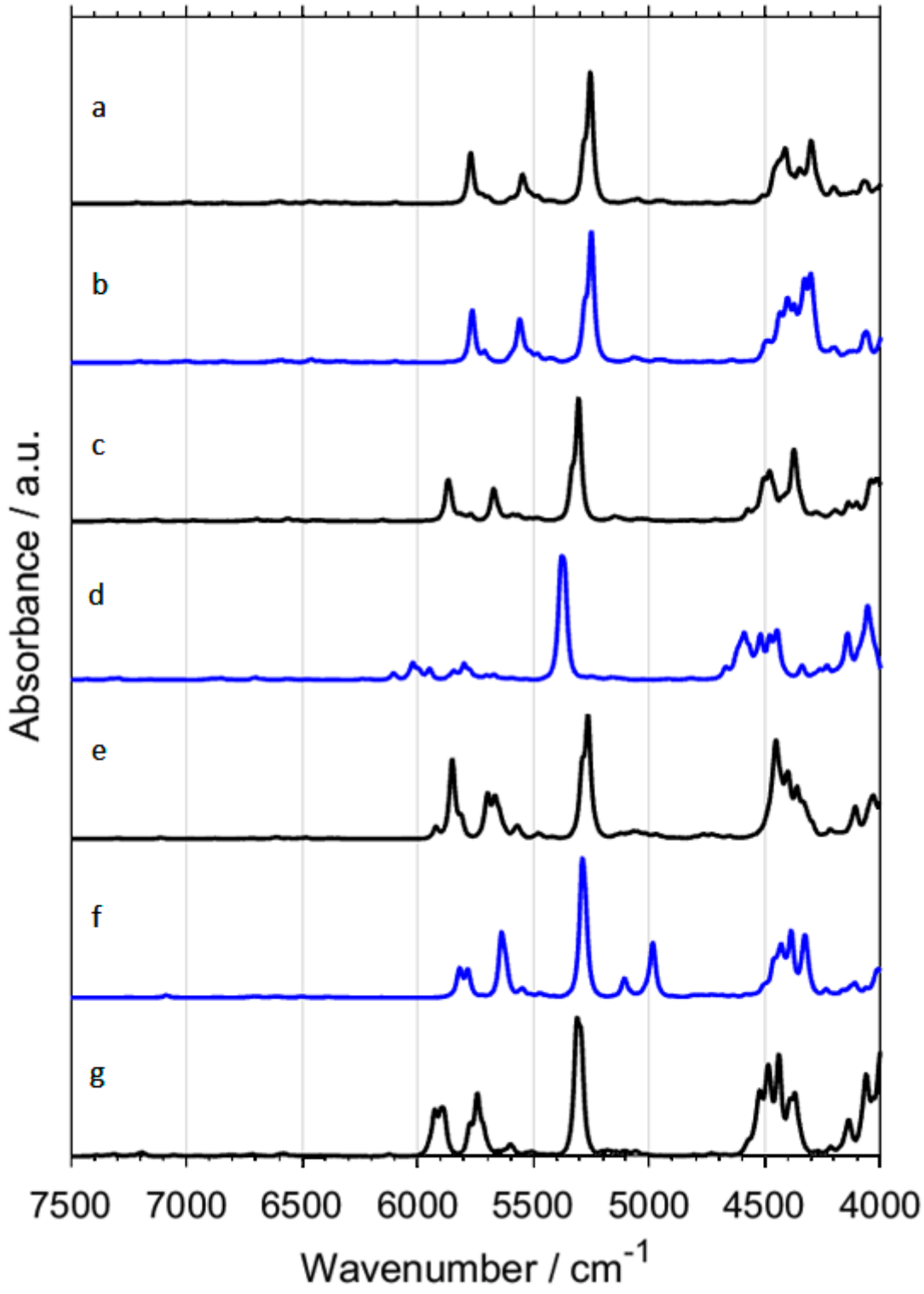

Figure S6. NIR spectra of CD_3CH_2OD calculated with GVPT2 method at different levels of electronic theory; (a) B3LYP-GD3BJ /6-31G(d,p); (b) B3LYP-GD3BJ /6-31G(d,p)//CPCM; (c) B2PLYP-GD3BJ/6-31G(d,p)//CPCM; (d) MP2/6-31G(d,p)//CPCM; (e) B3LYP-GD3BJ/SNST//CPCM; (f) B2PLYP-GD3BJ/def2-TZVP//CPCM; (g) MP2/aug-cc-pVTZ//CPCM.

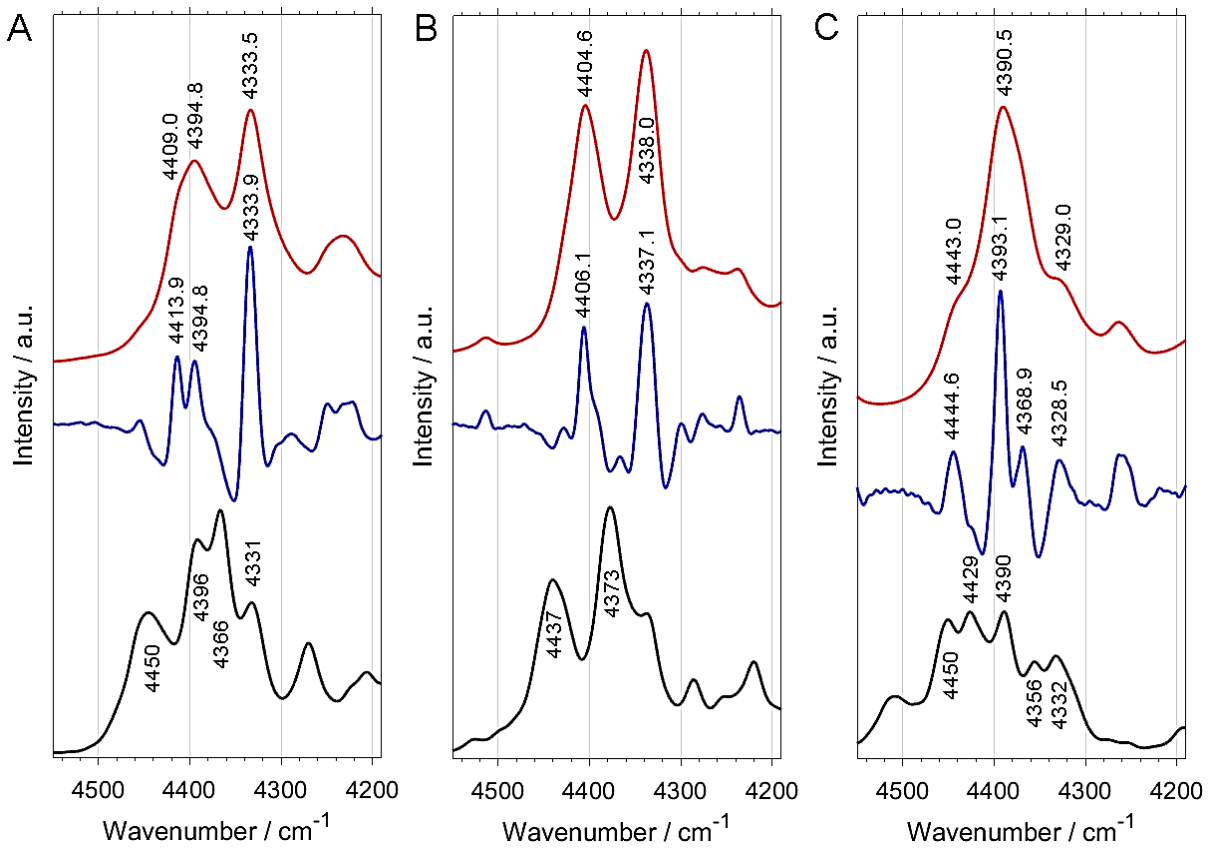

Figure S7. The details of NIR spectra of (A) CH_3CH_2OH; (B) CH_3CD_2OH; (C) CD_3CH_2OH in the 4550-4200 cm^{-1}. From up to bottom: experimental NIR spectrum (red line); second derivative spectrum, multiplied by -1 (blue line); theoretical (B2PLYP-GD3BJ/def2-TZVP//CPCM) spectrum (black line).

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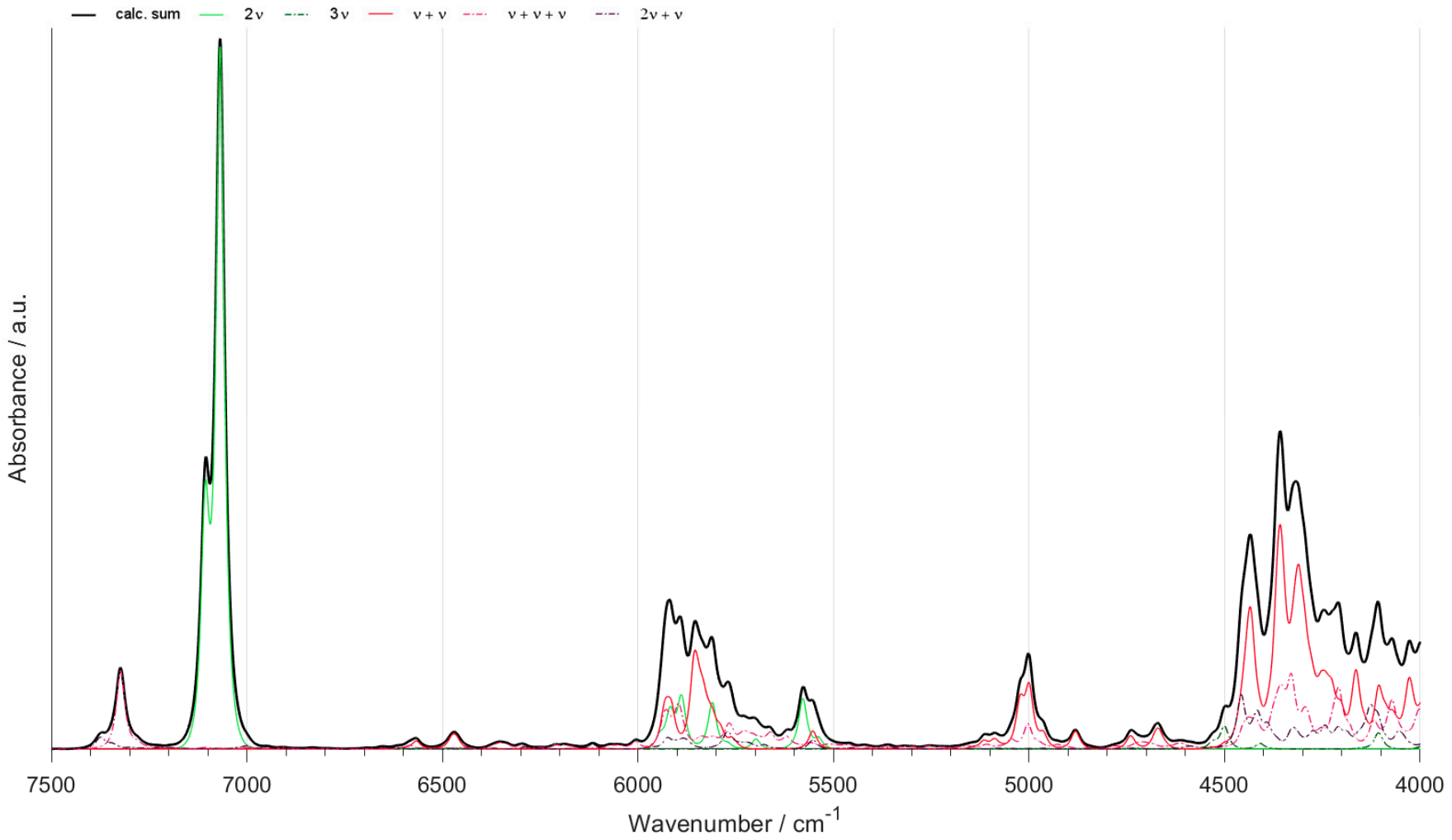

Figure S8. (Enlarged) NIR spectra of CH_3CH_2OH calculated with GVPT2 method at B3LYP-GD3BJ/6-31G(d,p) level of electronic theory

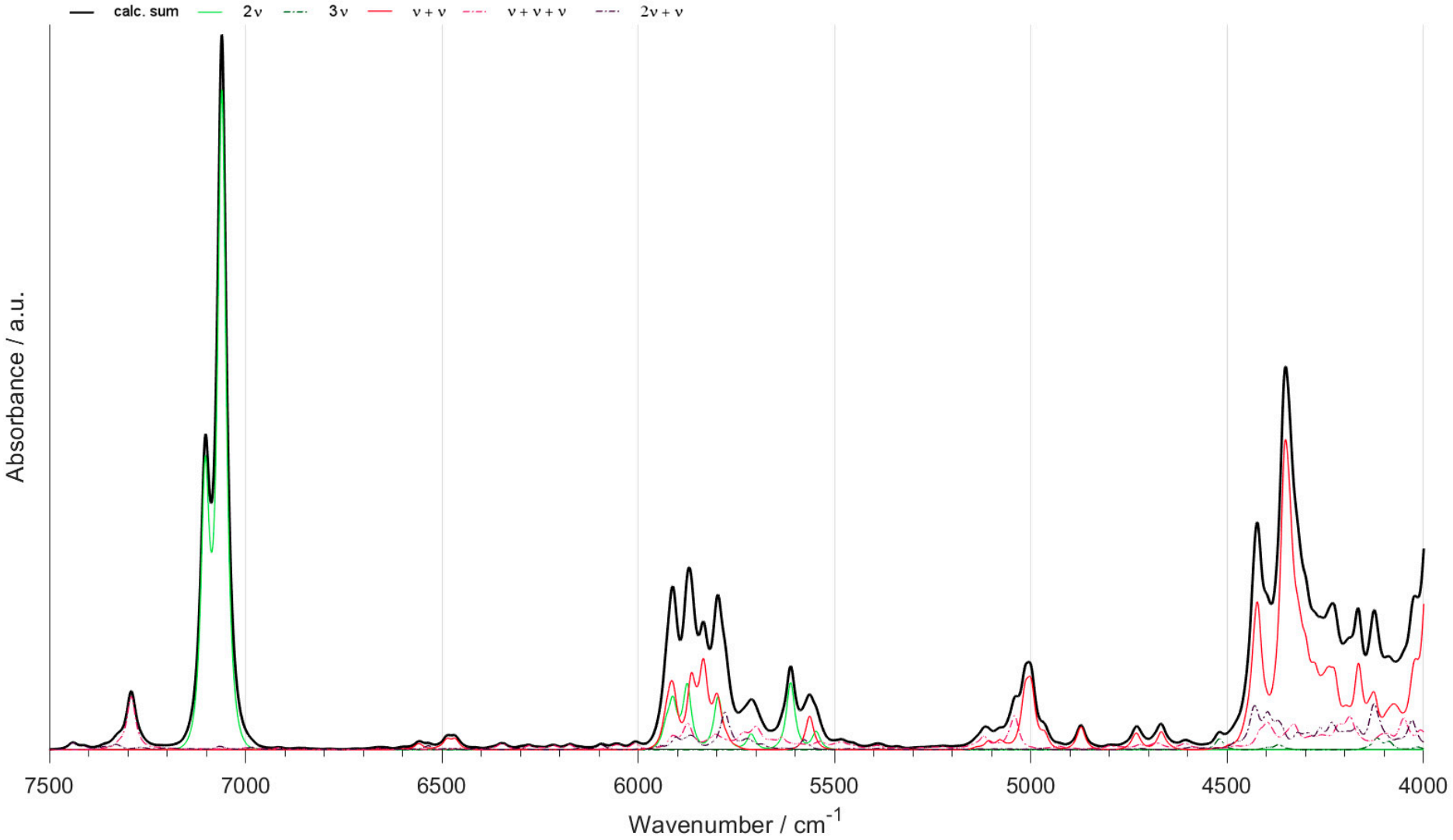

Figure S9. (High-resolution copy of Figure 1) NIR spectra of CH_3CH_2OH calculated with GVPT2 method at B3LYP-GD3BJ/6-31G(d,p)//CPCM level of electronic theory.

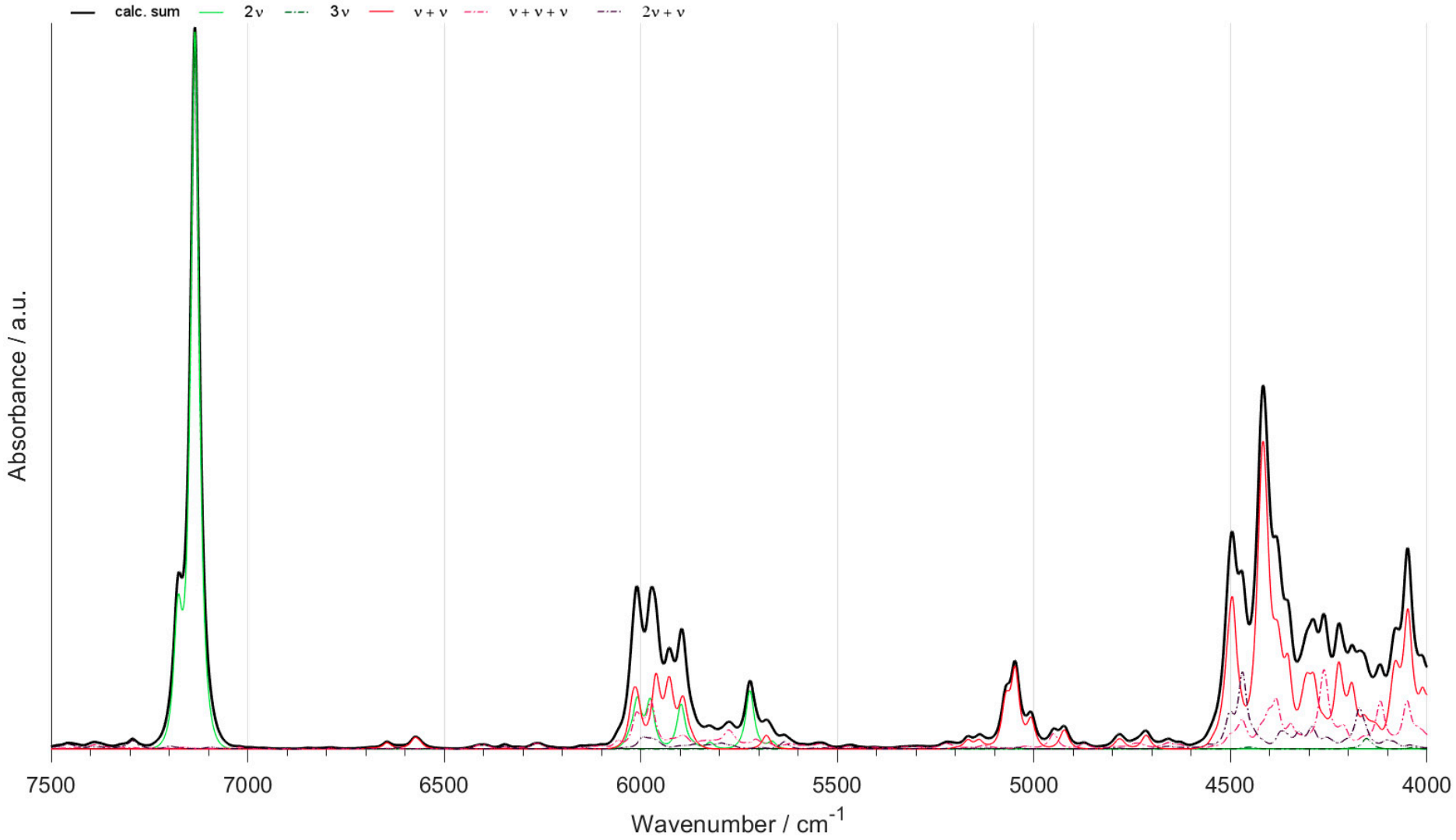

Figure S10. (High-resolution copy of Figure 1) NIR spectra of CH_3CH_2OH calculated with GVPT2 method at B2PLYP-GD3BJ/6-31G(d,p)//CPCM level of electronic theory.

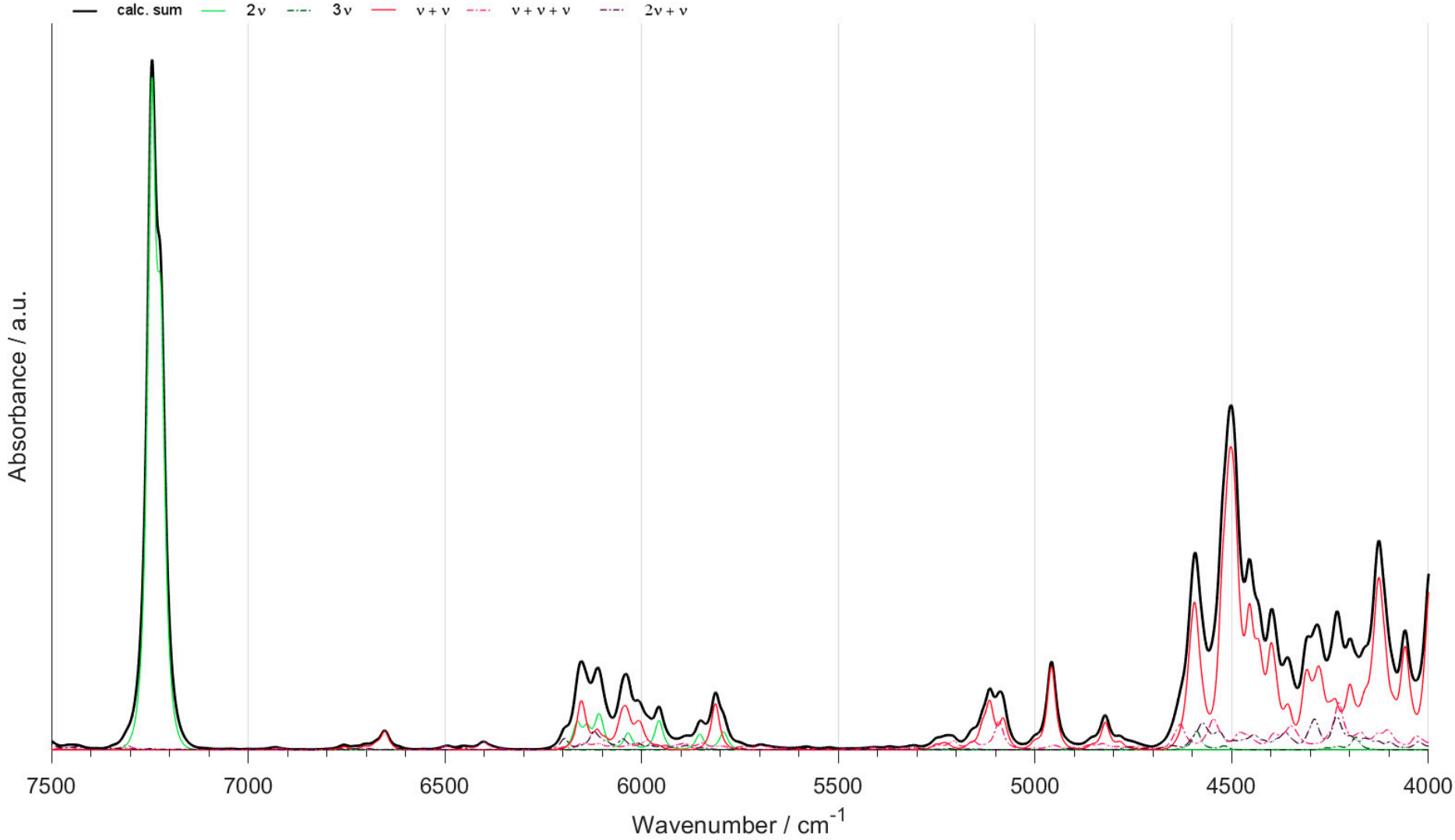

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Figure S11. (High-resolution copy of Figure 1) NIR spectra of CH_3CH_2OH calculated with GVPT2 method at MP2/6-31G(d,p)//CPCM level of electronic theory.

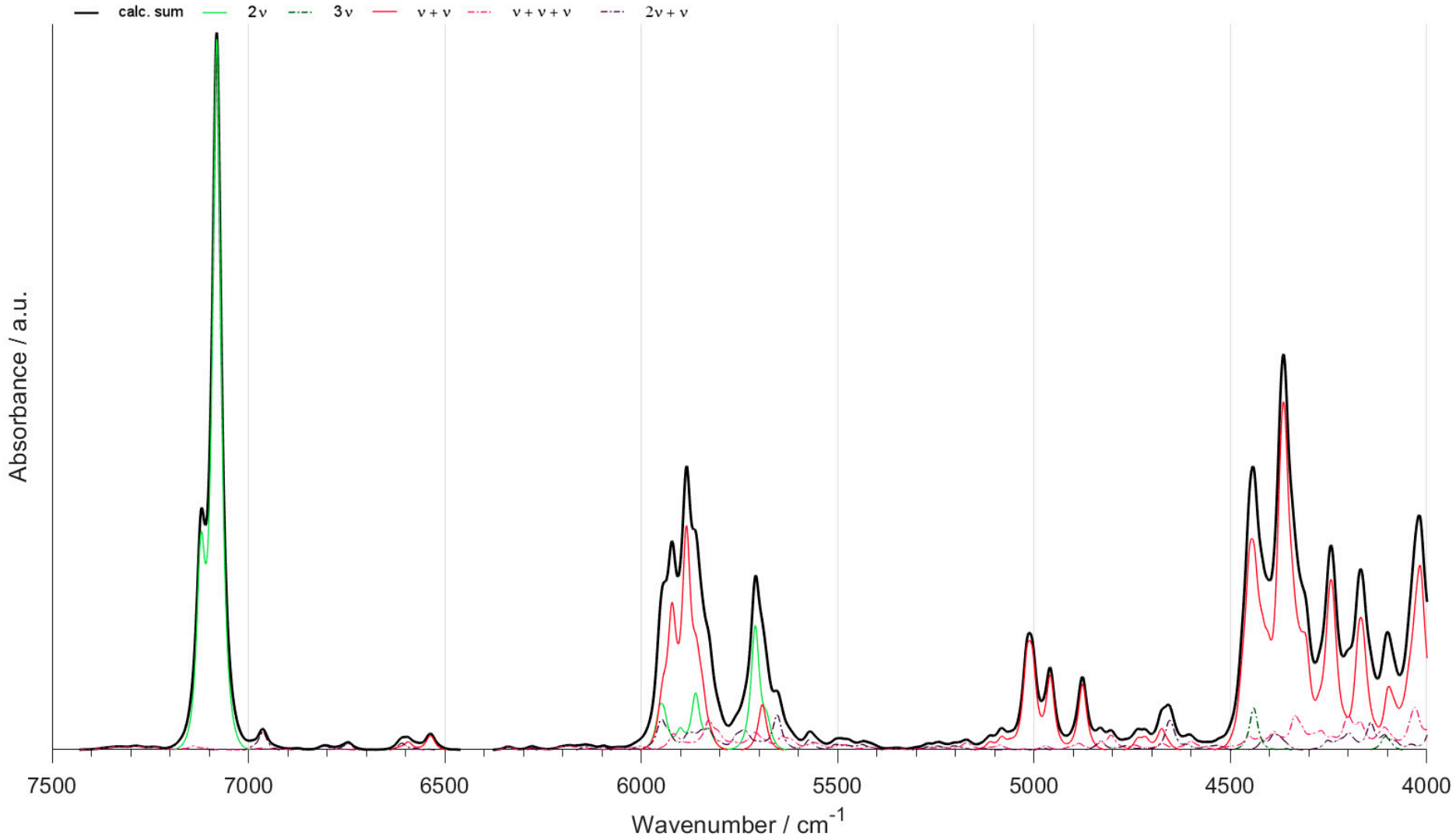

Figure S12. (High-resolution copy of Figure 1) NIR spectra of CH_3CH_2OH calculated with GVPT2 method at B3LYP-GD3BJ/SNST//CPCM level of electronic theory.

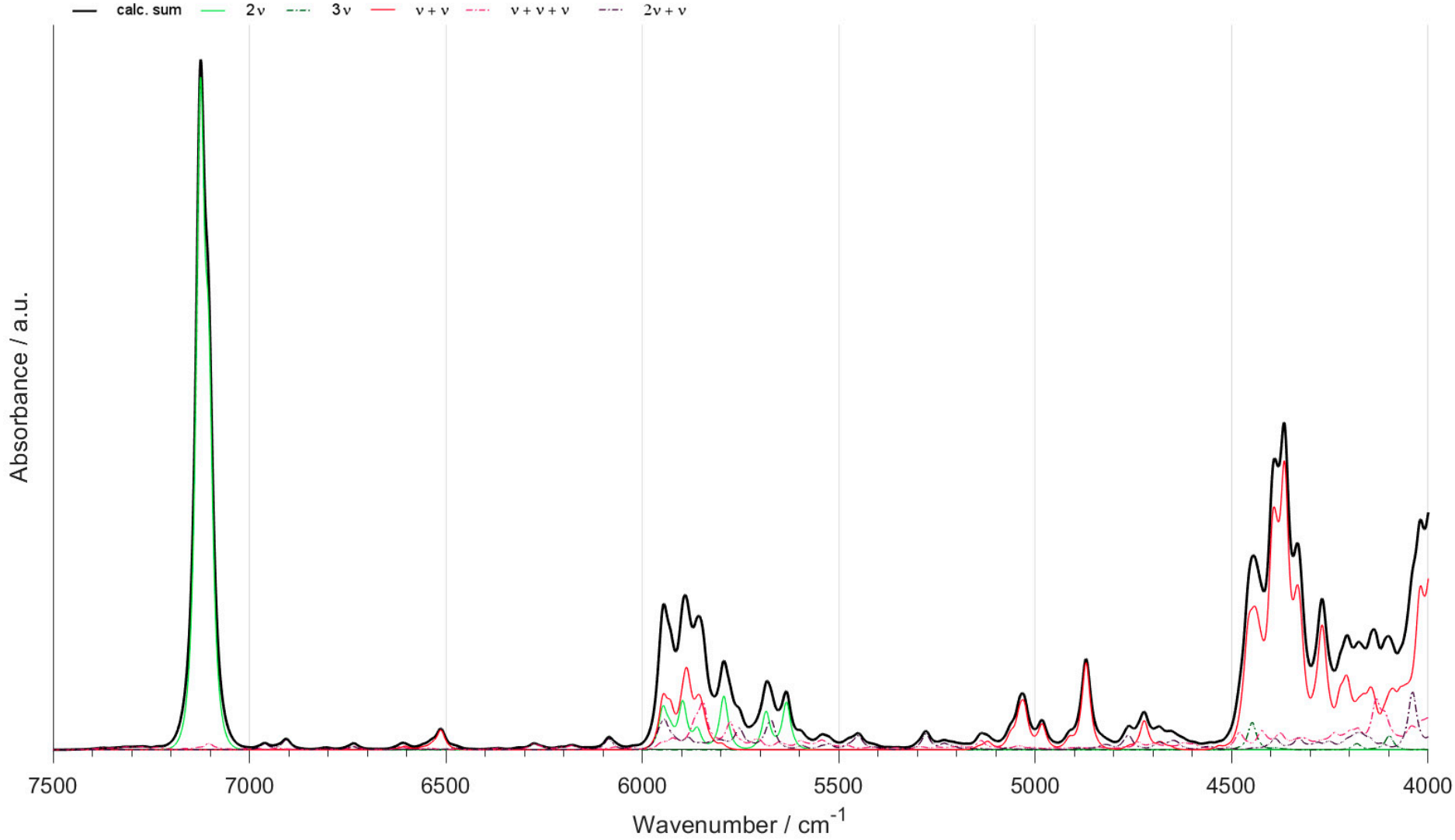

Figure S13. (High-resolution copy of Figure 1) NIR spectra of CH_3CH_2OH calculated with GVPT2 method at B2PLYP-GD3BJ/def2-TZVP//CPCM level of electronic theory.

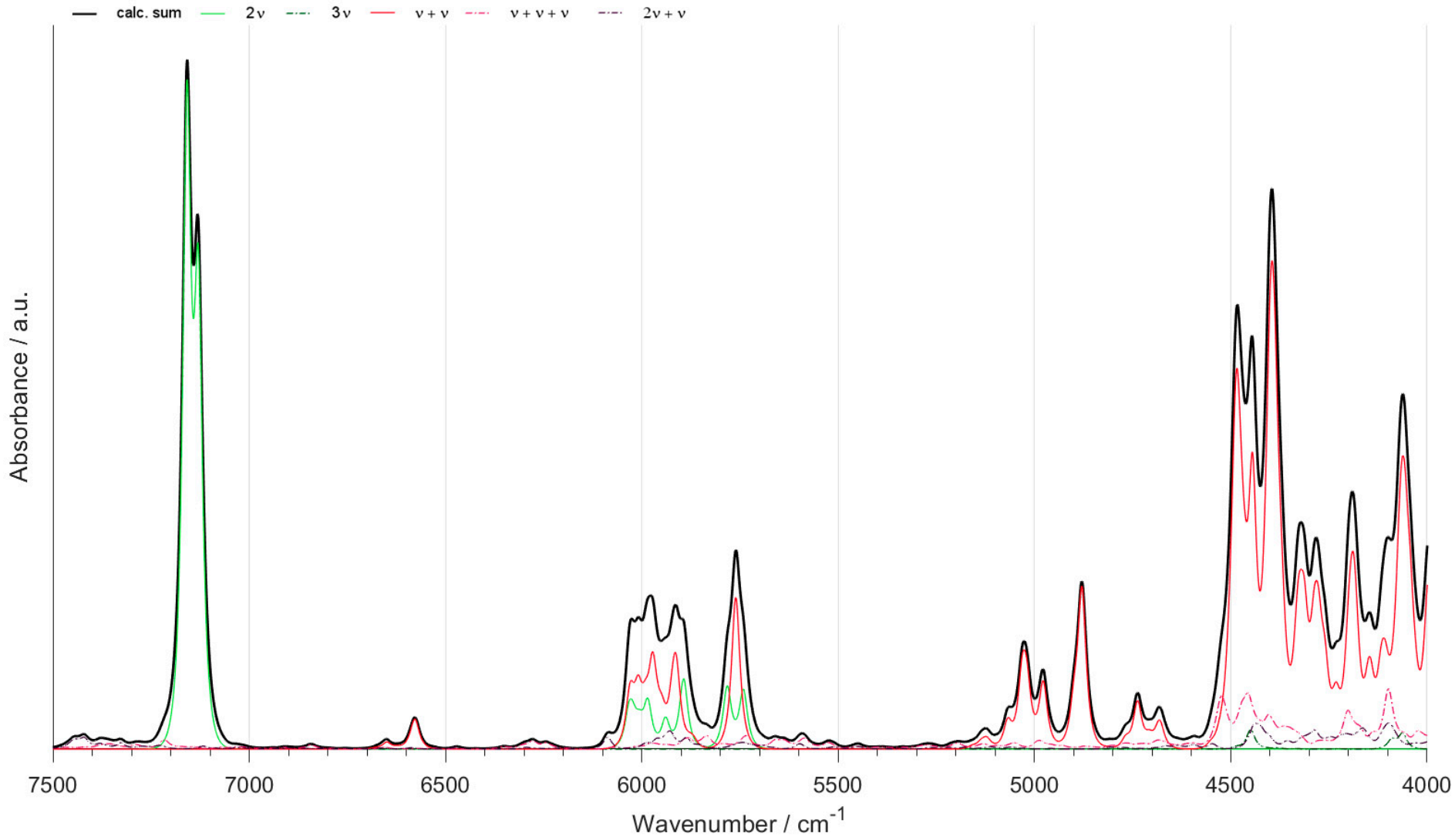

Figure S14. (High-resolution copy of Figure 1) NIR spectra of CH_3CH_2OH calculated with GVPT2 method at MP2/aug-cc-pVTZ//CPCM level of electronic theory.

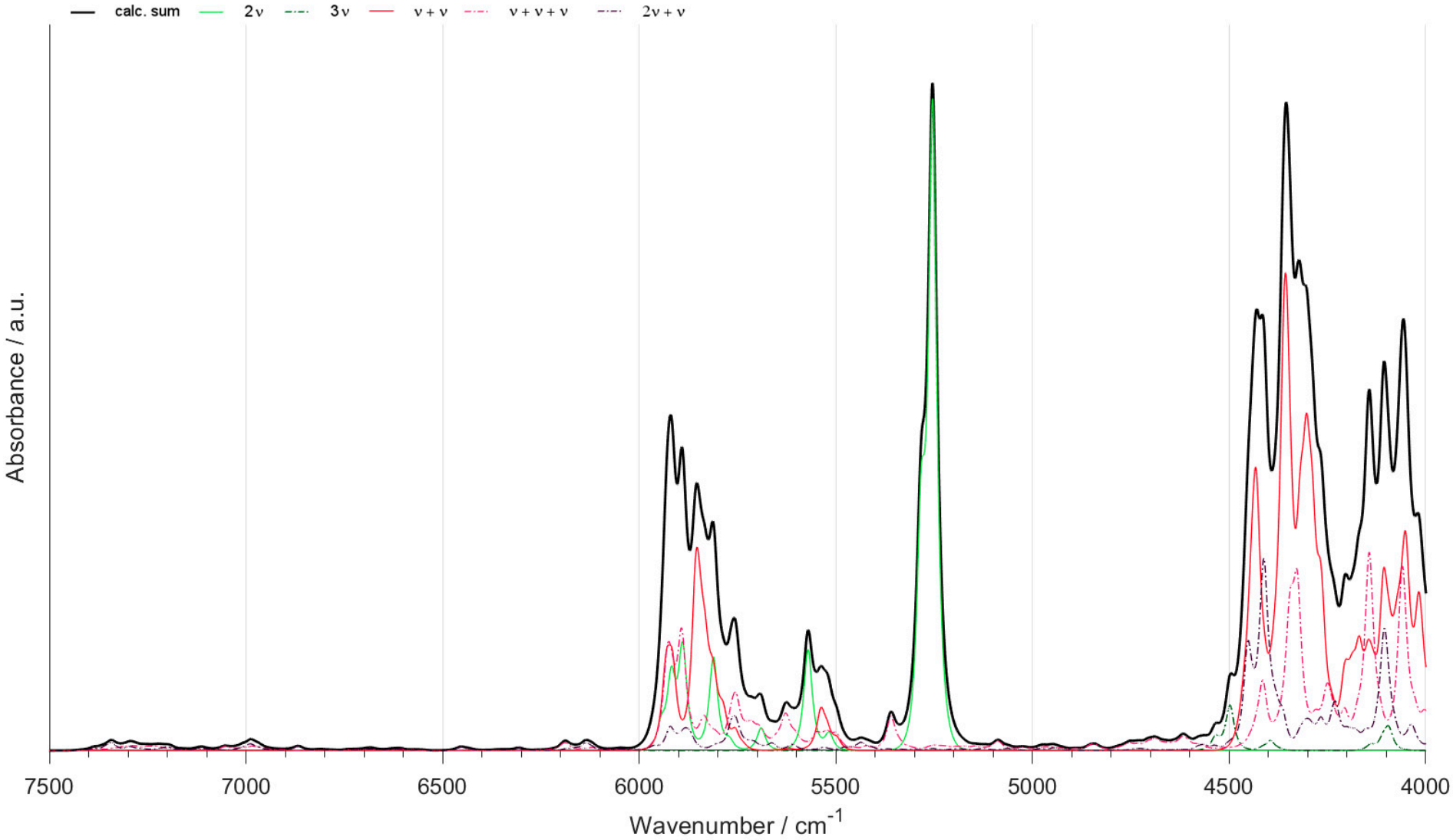

Figure S15. (High-resolution copy of Figure 2) NIR spectra of CH_3CH_2OD calculated with GVPT2 method at B3LYP-GD3BJ/6-31G(d,p) level of electronic theory.

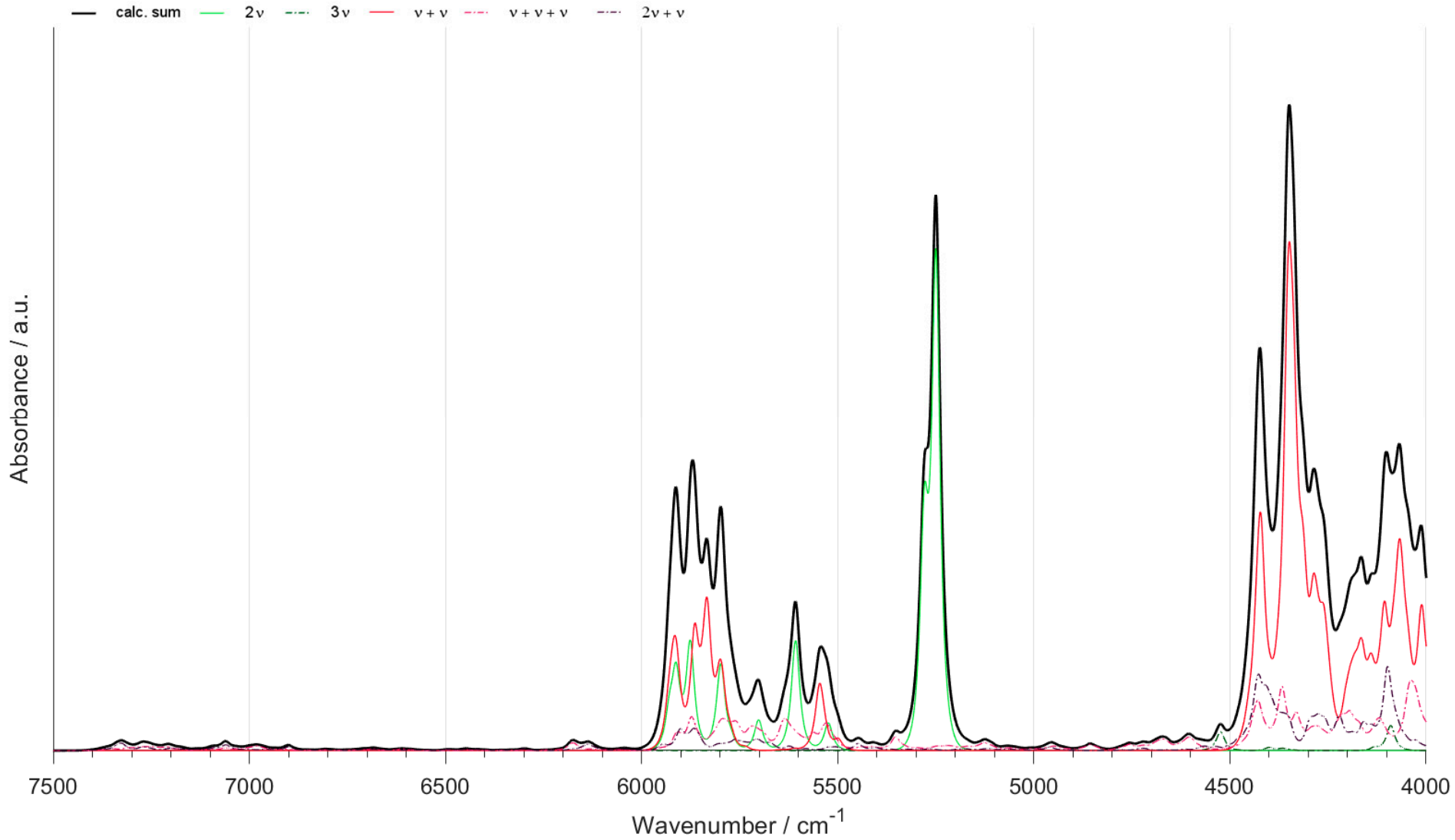

Figure S16. (High-resolution copy of Figure 2) NIR spectra of CH_3CH_2OD calculated with GVPT2 method at B3LYP-GD3BJ/6-31G(d,p)//CPCM level of electronic theory.

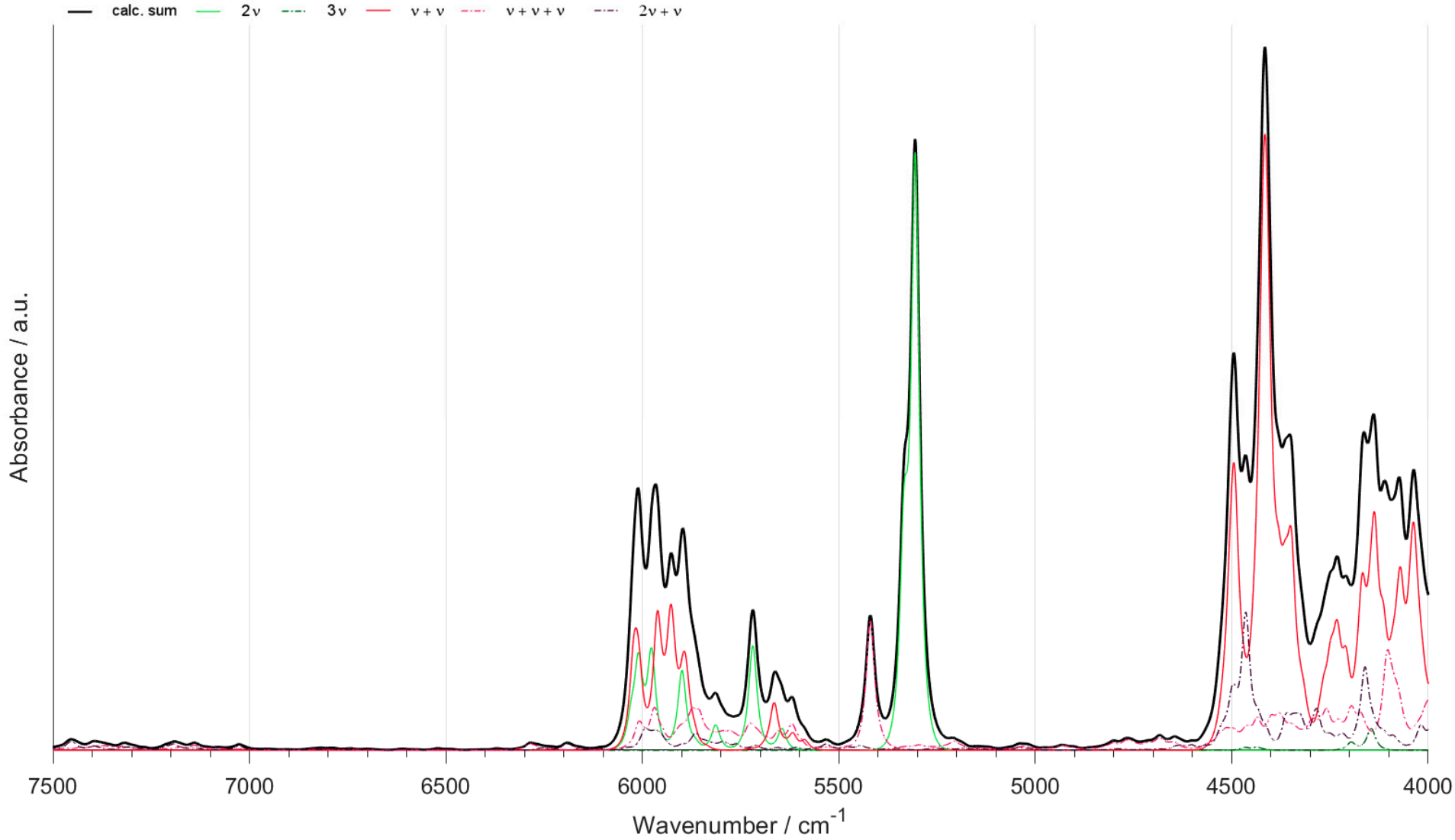

Figure S17. (High-resolution copy of Figure 2) NIR spectra of CH_3CH_2OD calculated with GVPT2 method at B2PLYP-GD3BJ/6-31G(d,p)//CPCM level of electronic theory.

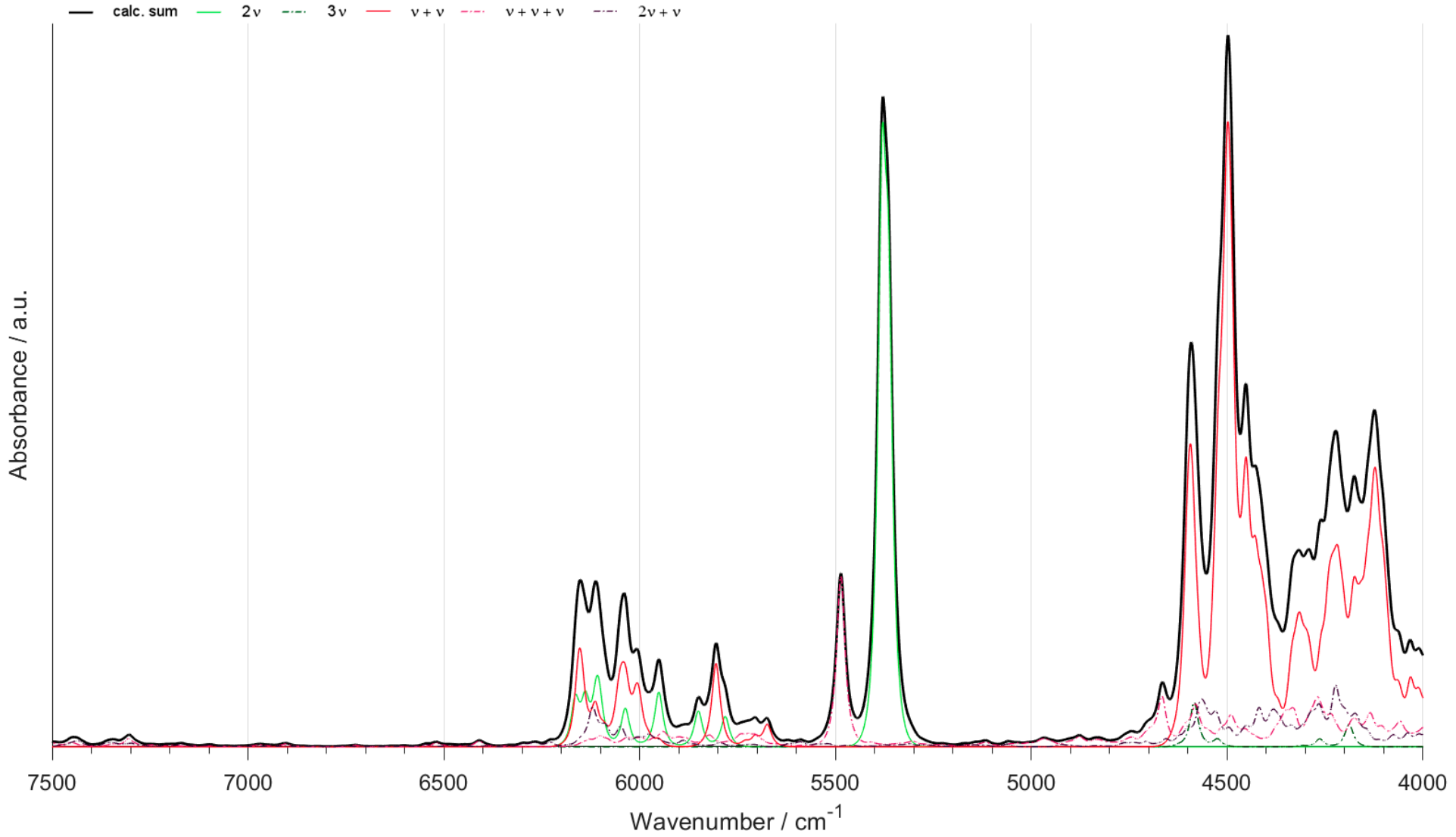

Figure S18. (High-resolution copy of Figure 2) NIR spectra of CH_3CH_2OD calculated with GVPT2 method at MP2/6-31G(d,p)//CPCM t level of electronic theory.

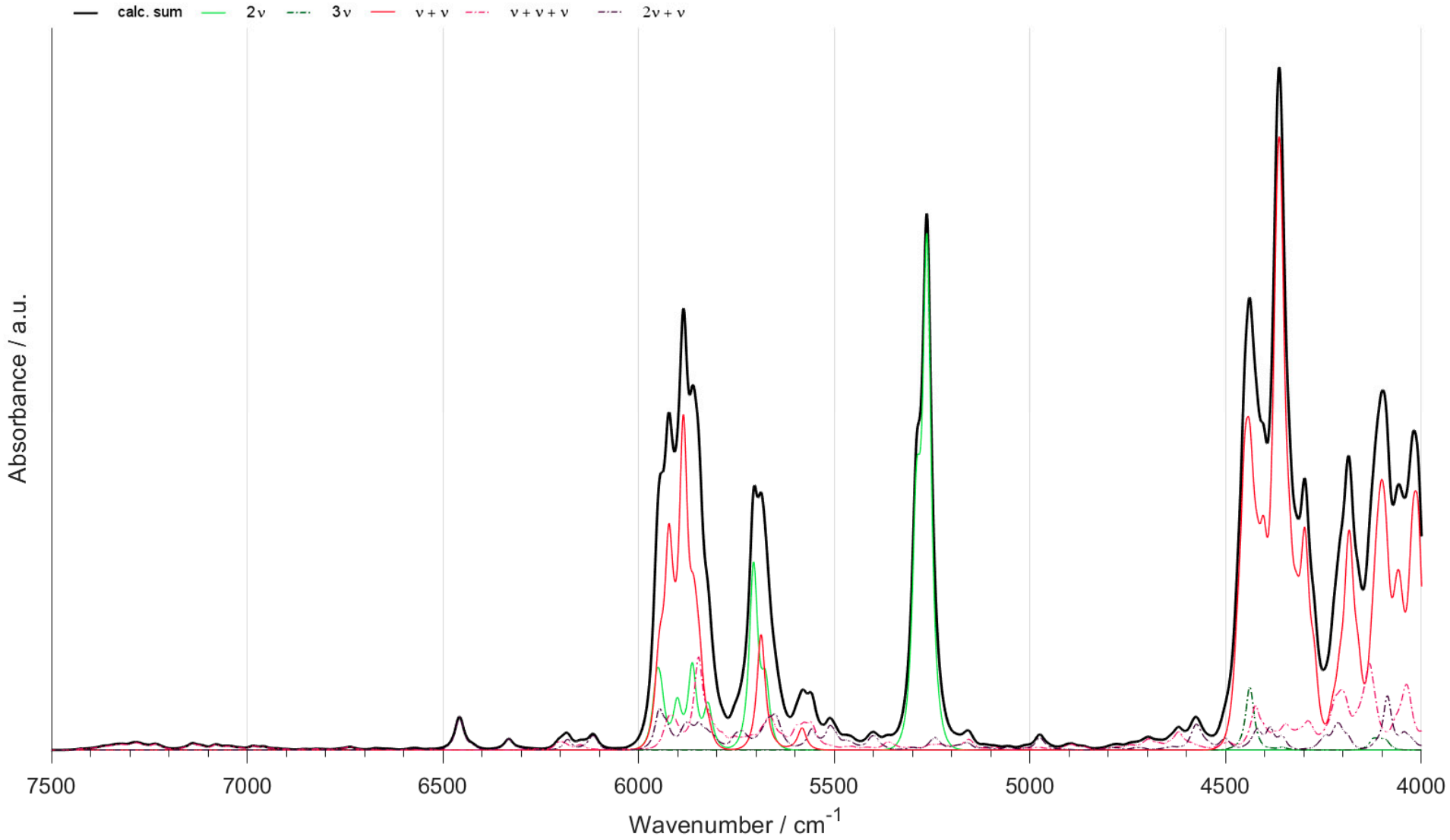

Figure S19. (High-resolution copy of Figure 2) NIR spectra of CH_3CH_2OD calculated with GVPT2 method at B3LYP-GD3BJ/SNST//CPCM level of electronic theory.

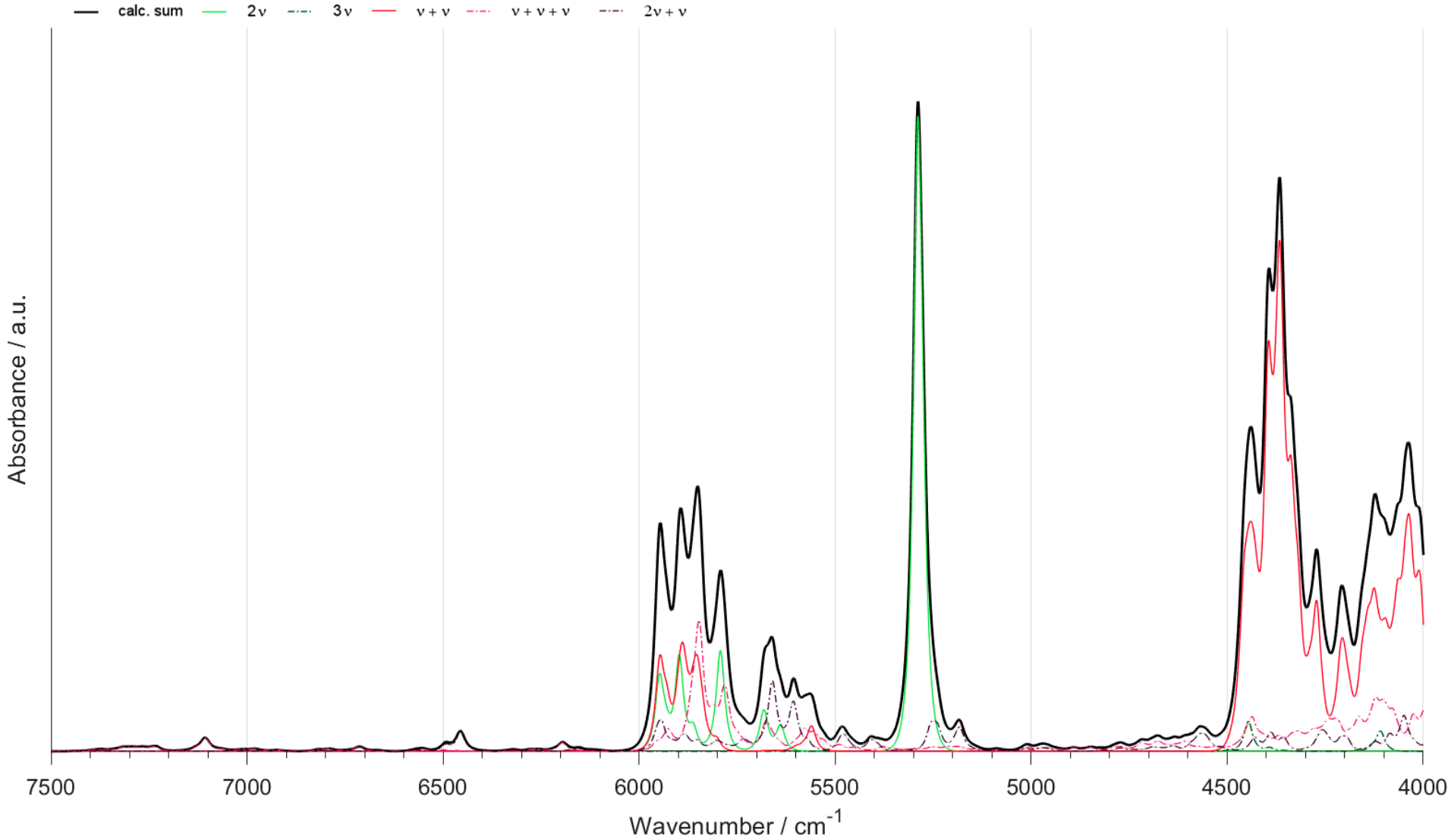

Figure S20. (High-resolution copy of Figure 2) NIR spectra of CH_3CH_2OD calculated with GVPT2 method at B2PLYP-GD3BJ/def2-TZVP//CPCM level of electronic theory.

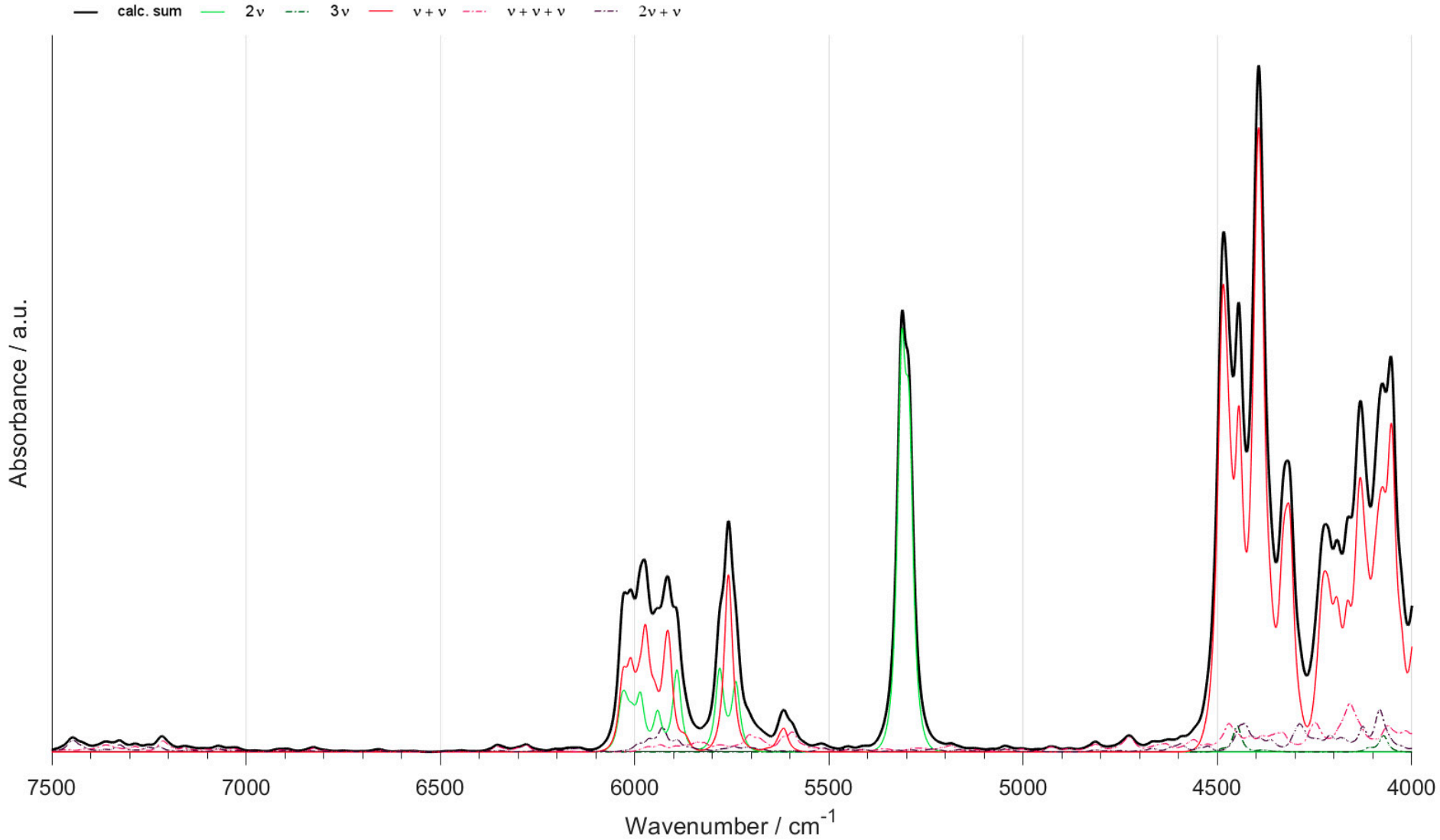

Figure S21. (High-resolution copy of Figure 2) NIR spectra of CH_3CH_2OD calculated with GVPT2 method at MP2/aug-cc-pVTZ//CPCM level of electronic theory.

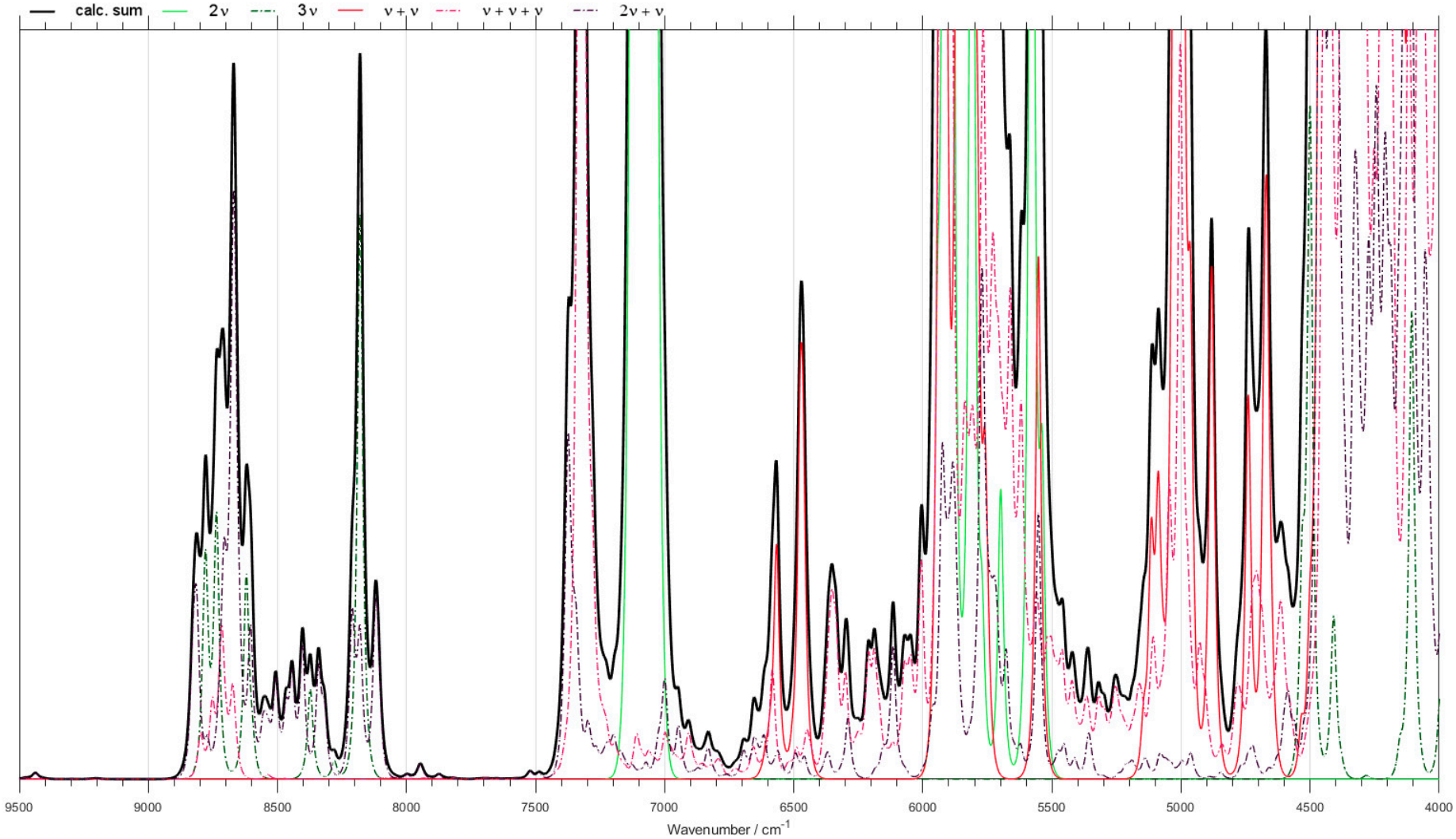

Figure S22. (High-resolution copy of Figure 3) Contributions from minor bands in NIR spectra of CH_3CH_2OH calculated with GVPT2 method at B3LYP-GD3BJ /6-31G(d,p) level of electronic theory.

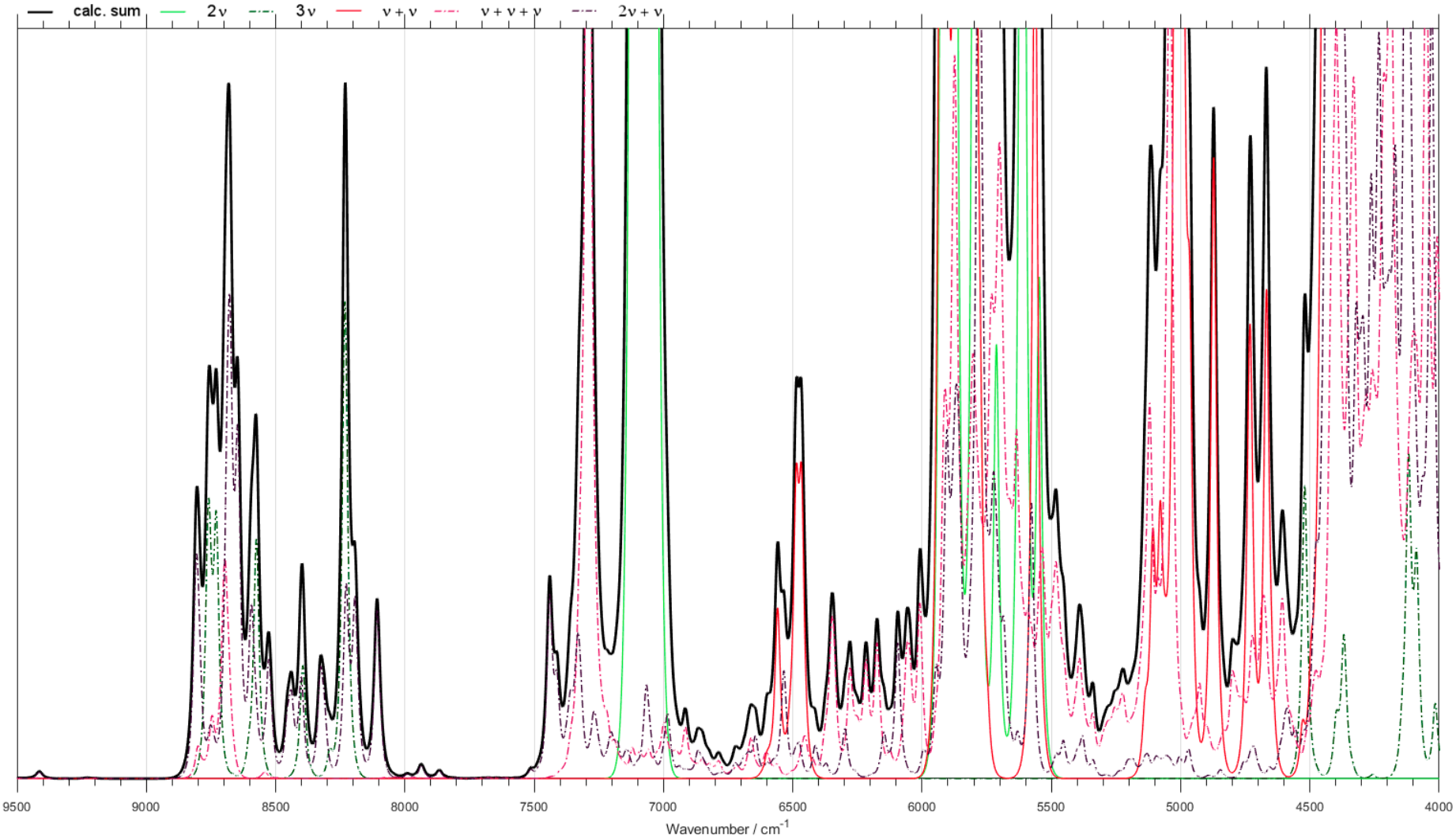

Figure S23. (High-resolution copy of Figure 3) Contributions from minor bands in NIR spectra of CH_3CH_2OH calculated with GVPT2 method at B3LYP-GD3BJ /6-31G(d,p)//CPCM level of electronic theory.

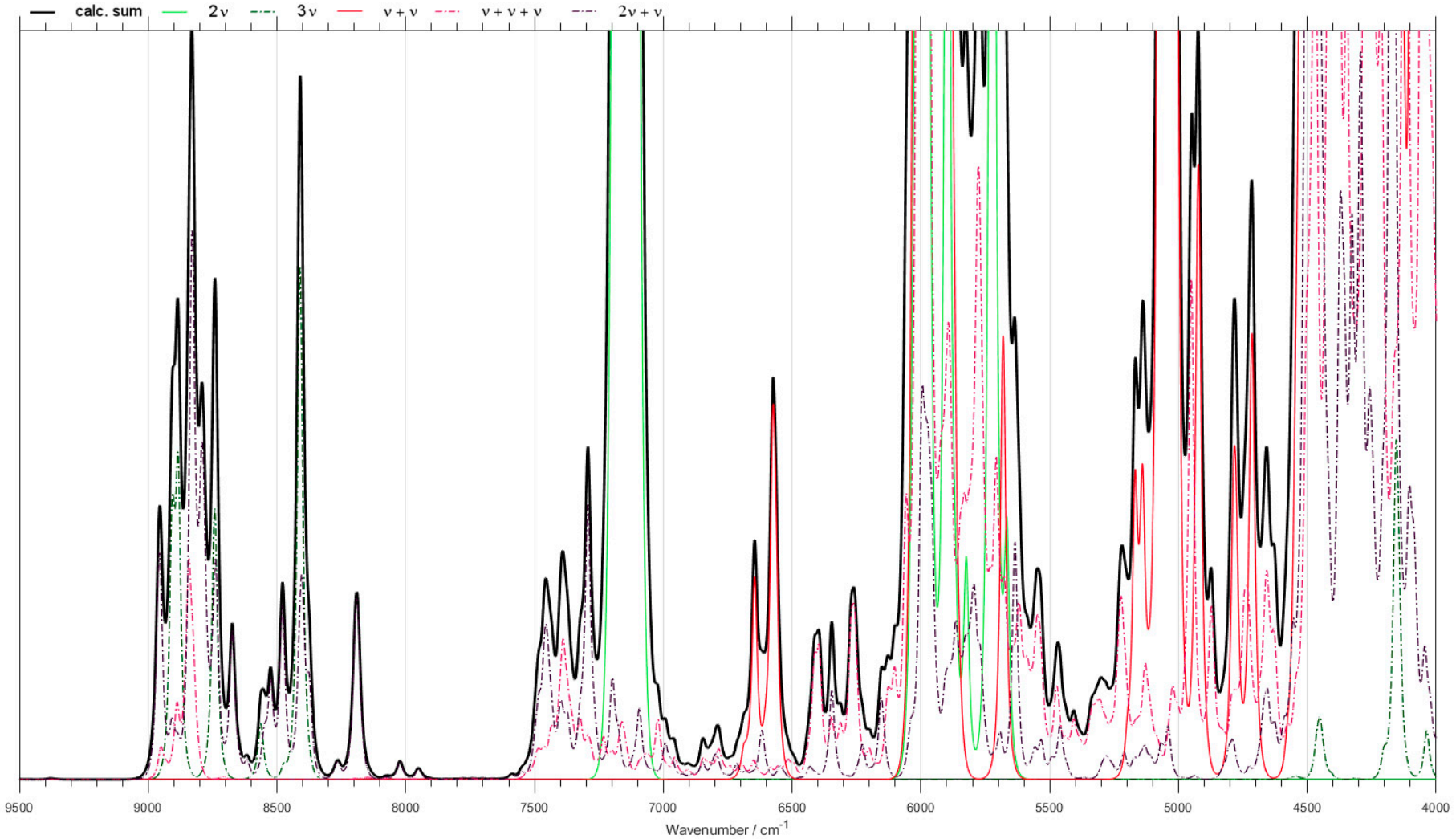

Figure S24. (High-resolution copy of Figure 3) Contributions from minor bands in NIR spectra of CH_3CH_2OH calculated with GVPT2 method at B2PLYP-GD3BJ/6-31G(d,p)//CPCM level of electronic theory.

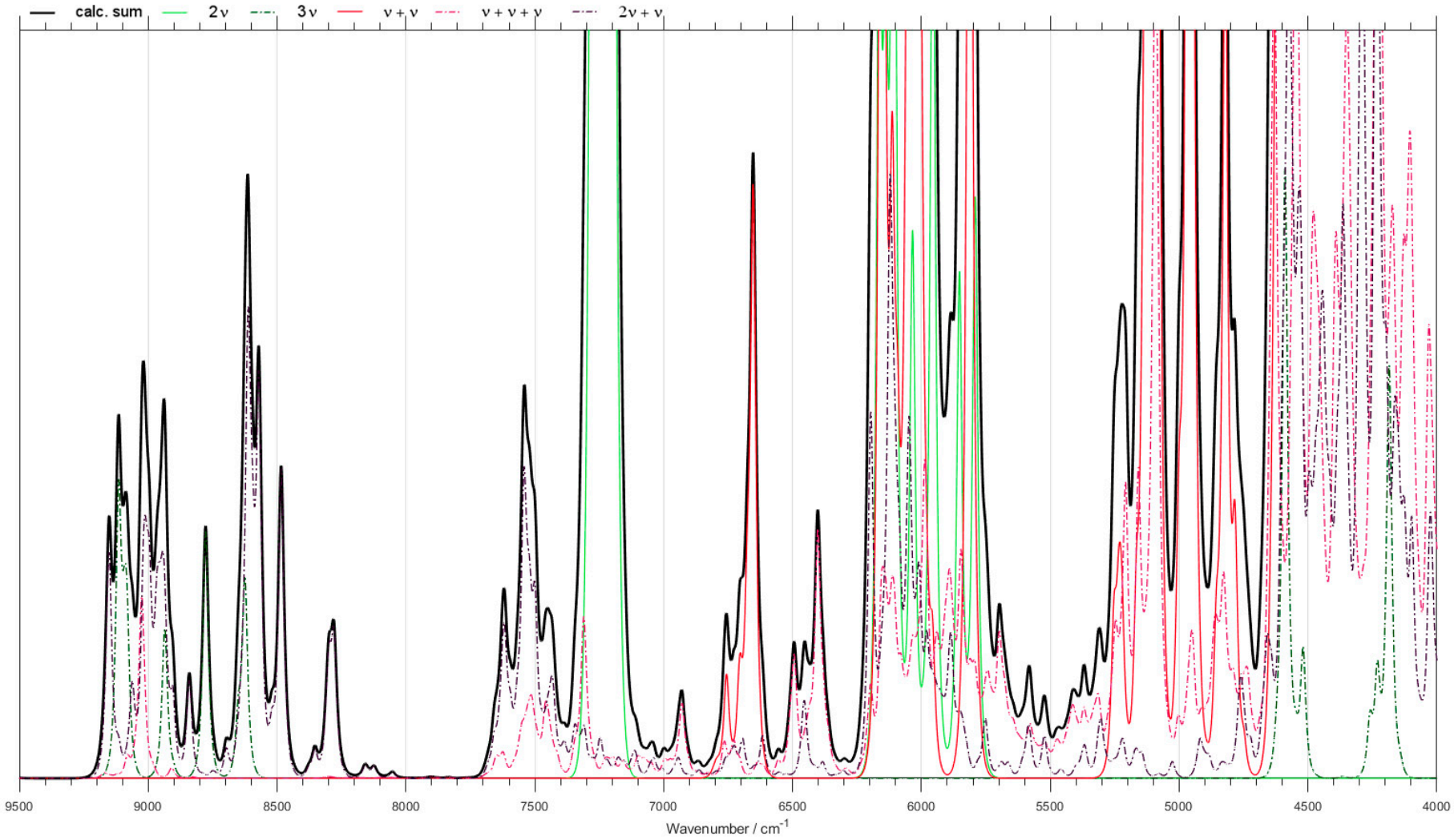

Figure S25. (High-resolution copy of Figure 2) Contributions from minor bands in NIR spectra of CH_3CH_2OH calculated with GVPT2 method at MP2/6-31G(d,p)//CPCM level of electronic theory.

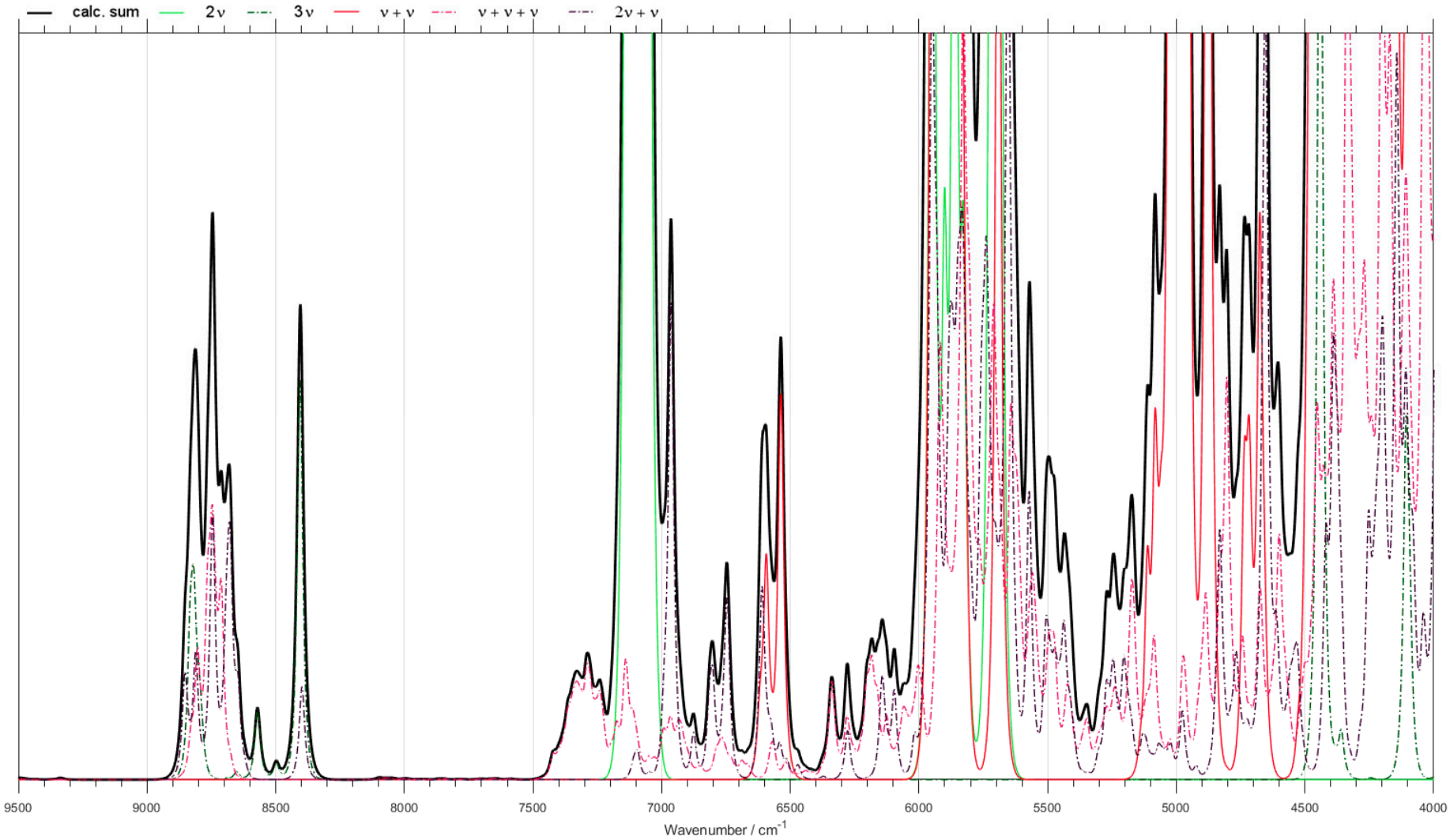

Figure S26. (High-resolution copy of Figure 3) Contributions from minor bands in NIR spectra of CH_3CH_2OH calculated with GVPT2 method at B3LYP-GD3BJ/SNST//CPCM level of electronic theory.

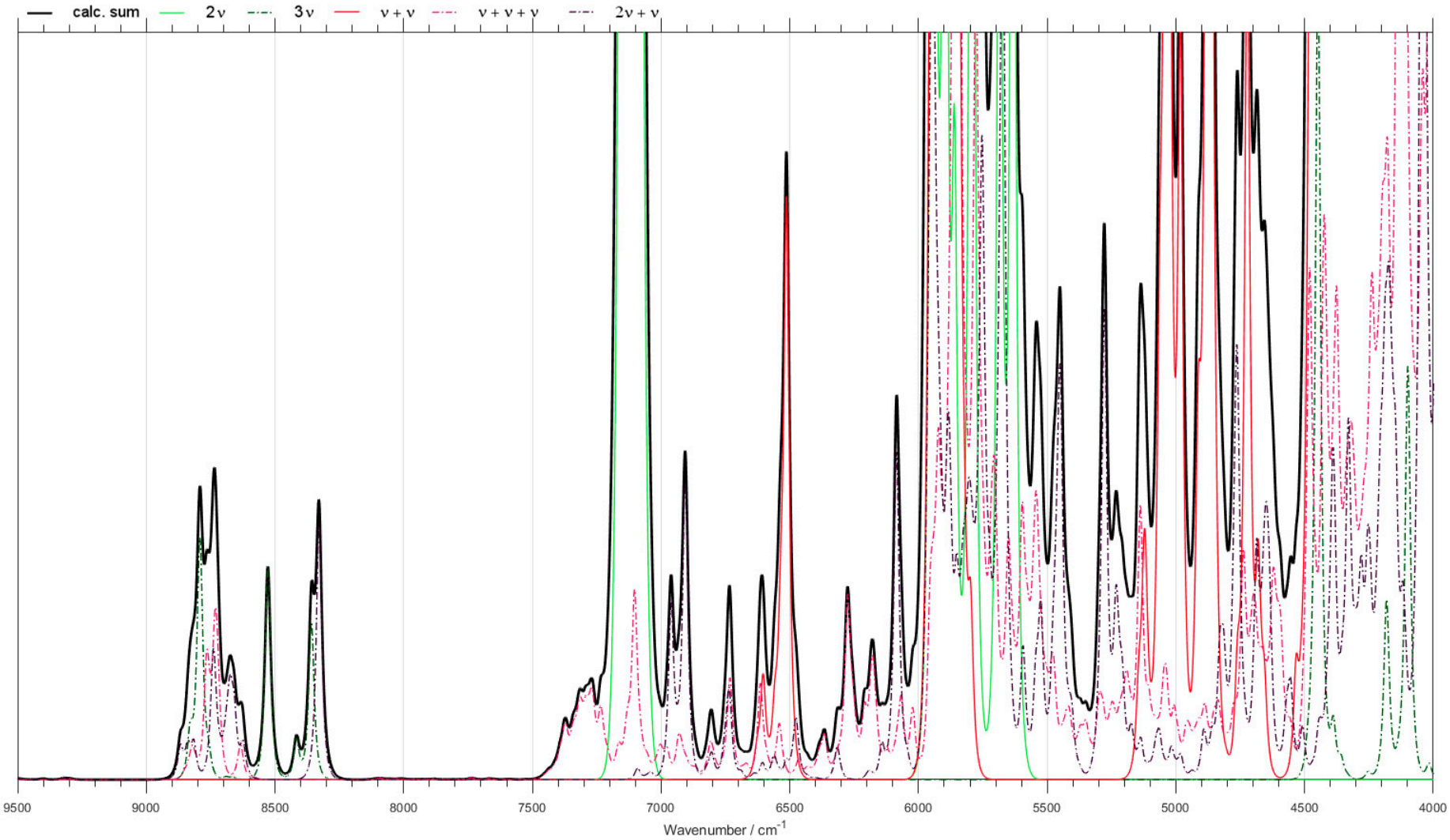

Figure S27. (High-resolution copy of Figure 3) Contributions from minor bands in NIR spectra of CH_3CH_2OH calculated with GVPT2 method at B2PLYP-GD3BJ/def2-TZVP//CPCM level of electronic theory.

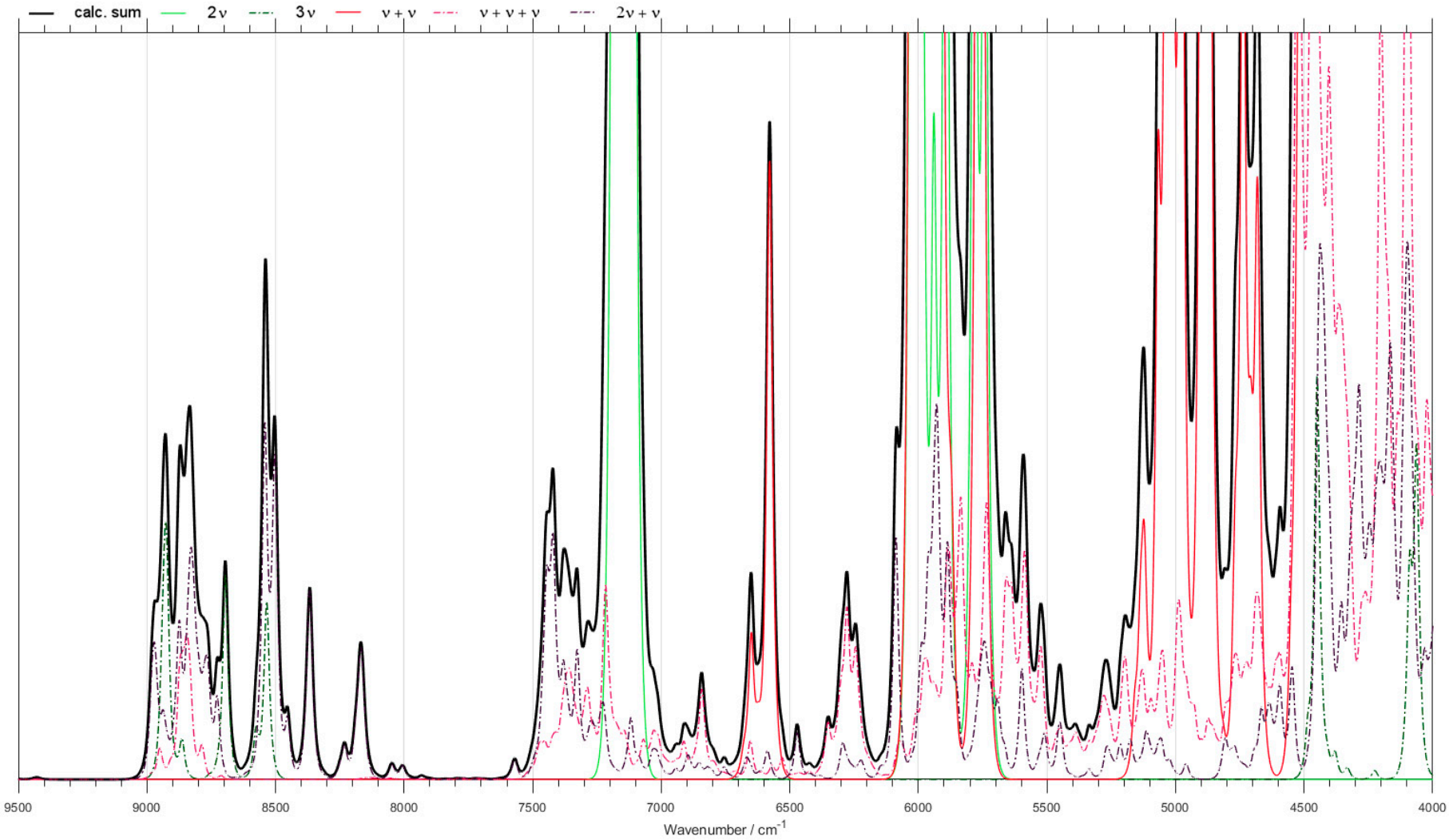

Figure S28. (High-resolution copy of Figure 3) Contributions from minor bands in NIR spectra of CH_3CH_2OH calculated with GVPT2 method at MP2/aug-cc-pVTZ//CPCM level of electronic theory.

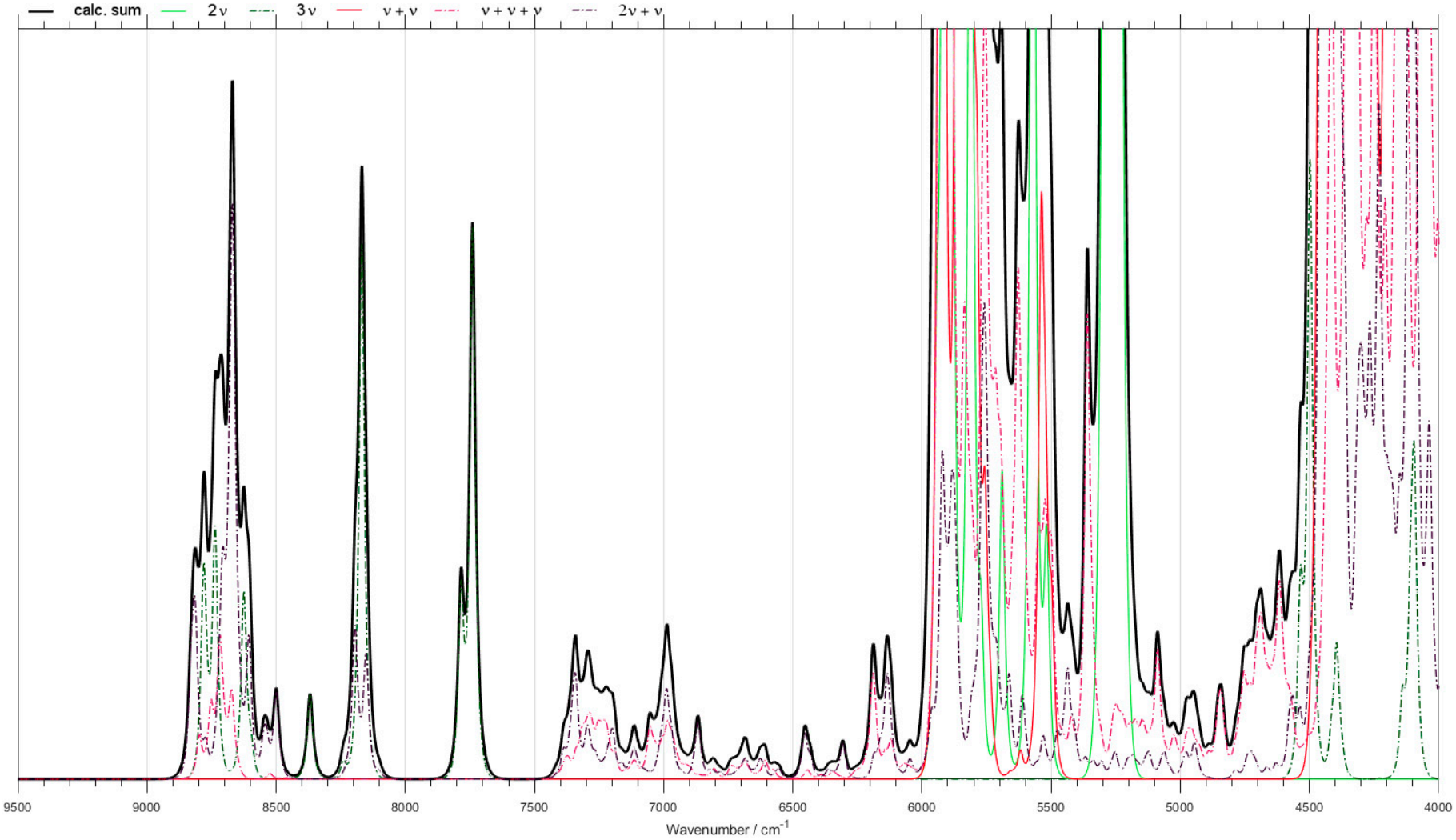

Figure S29. (High-resolution copy of Figure 4) Contributions from minor bands in NIR spectra of CH_3CH_2OD calculated with GVPT2 method at B3LYP-GD3BJ /6-31G(d,p) level of electronic theory.

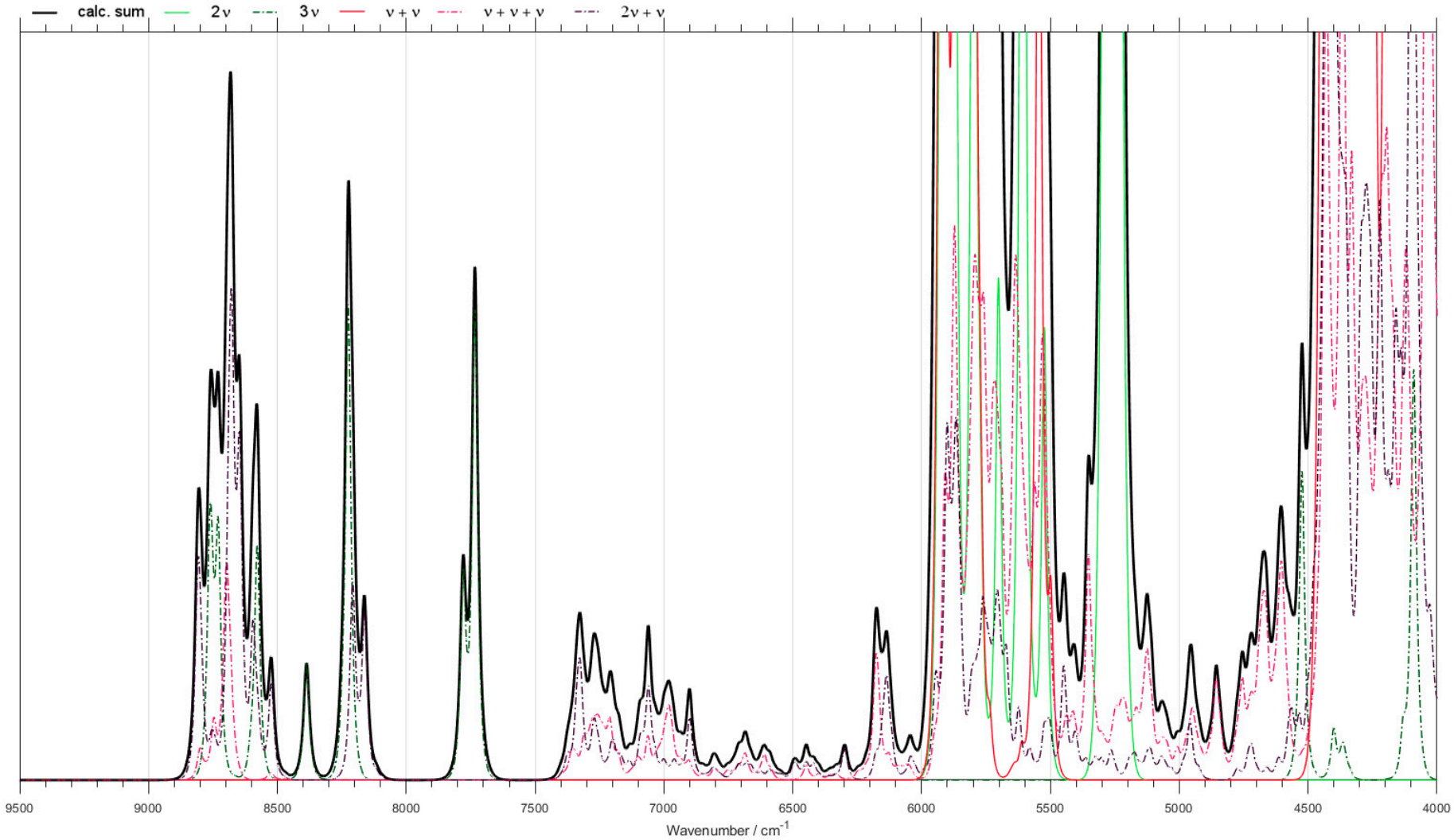

Figure S30. (High-resolution copy of Figure 4) Contributions from minor bands in NIR spectra of CH_3CH_2OD calculated with GVPT2 method at B3LYP-GD3BJ /6-31G(d,p)//CPCM level of electronic theory.

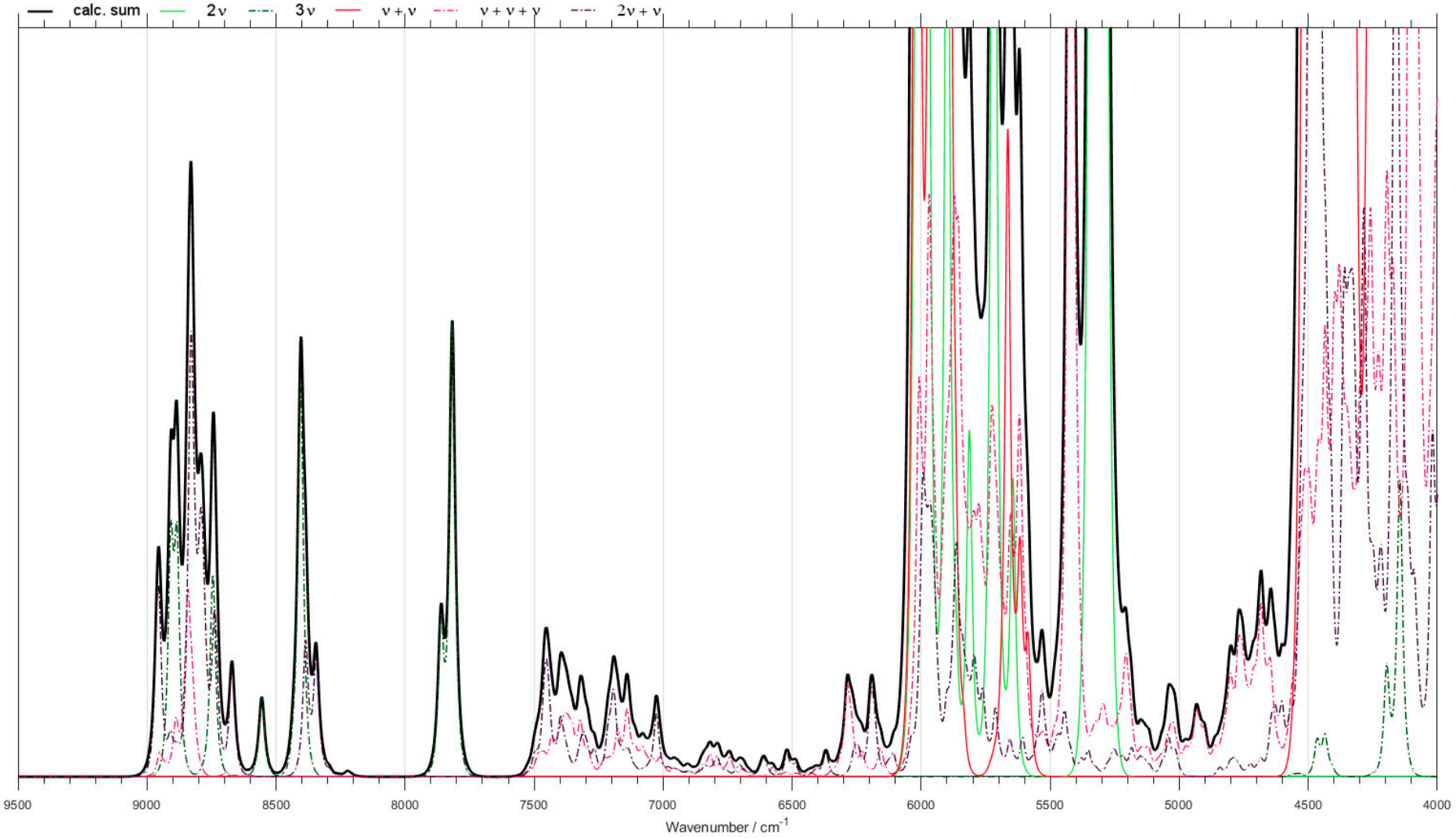

Figure S31. (High-resolution copy of Figure 4) Contributions from minor bands in NIR spectra of CH_3CH_2OD calculated with GVPT2 method at B2PLYP-GD3BJ/6-31G(d,p)//CPCM level of electronic theory.

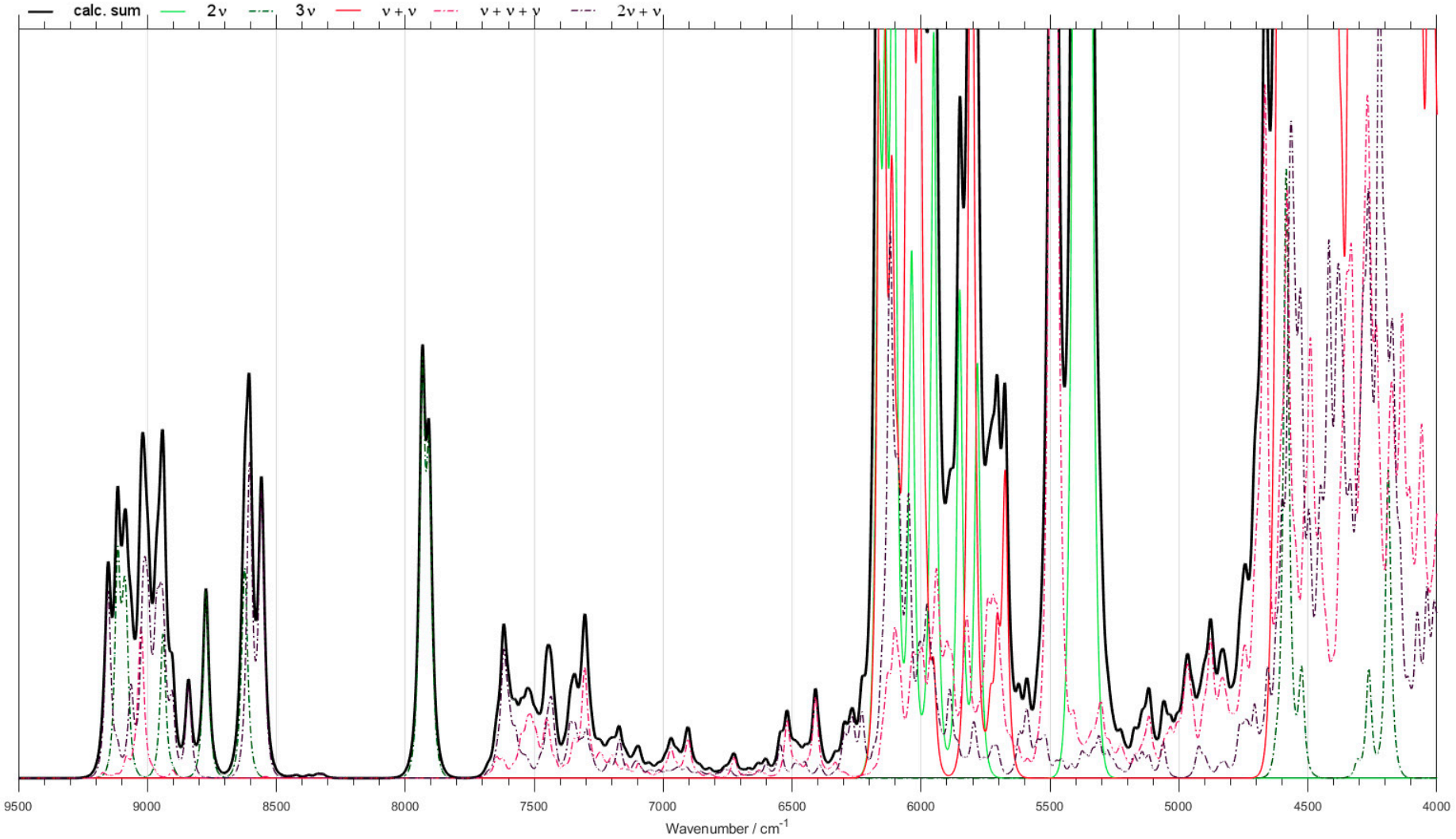

Figure S32. (High-resolution copy of Figure 4) Contributions from minor bands in NIR spectra of CH_3CH_2OD calculated with GVPT2 method at MP2/6-31G(d,p)//CPCM level of electronic theory.

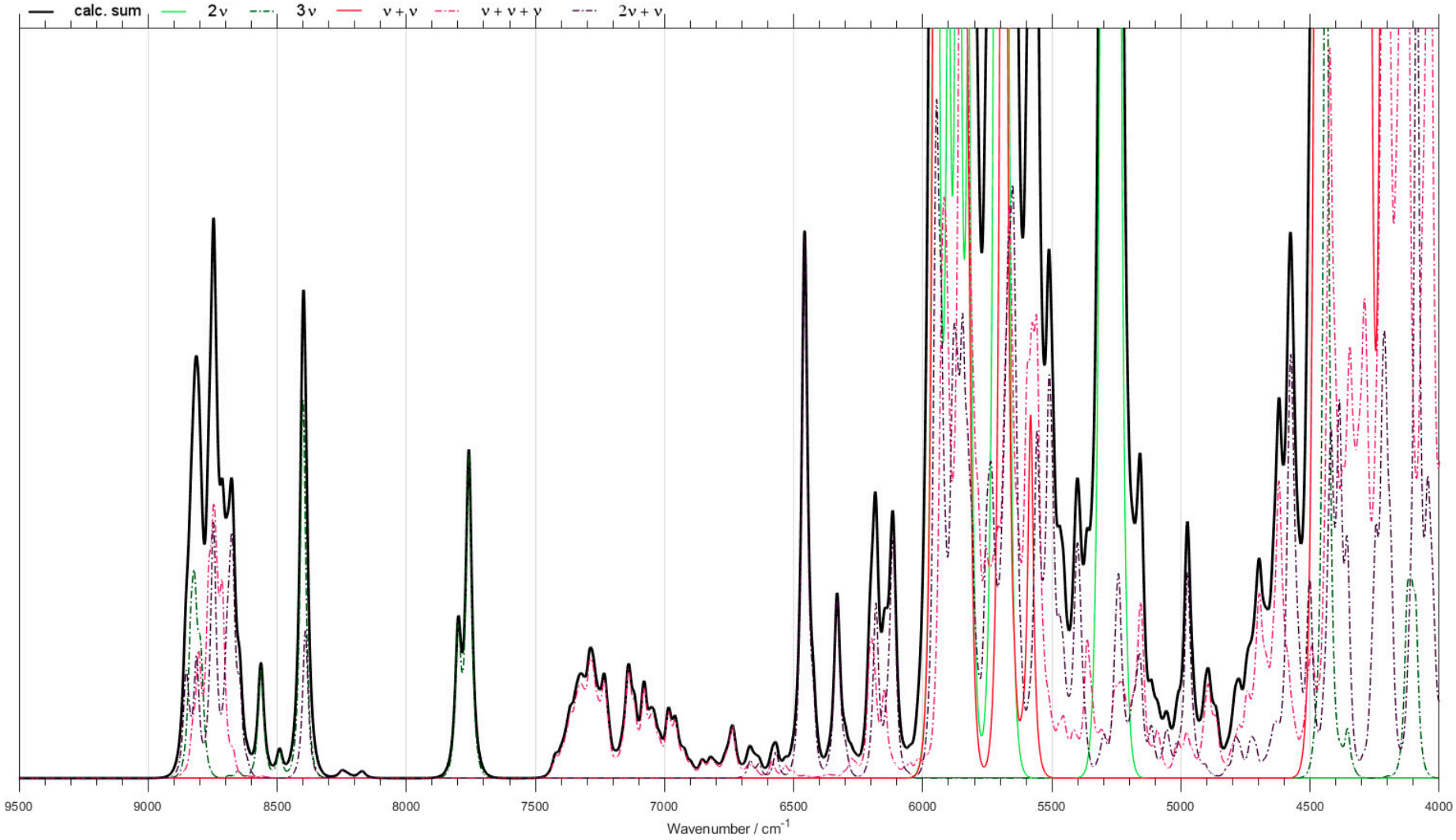

Figure S33. (High-resolution copy of Figure 4) Contributions from minor bands in NIR spectra of CH_3CH_2OD calculated with GVPT2 method at B3LYP-GD3BJ/SNST//CPCM level of electronic theory.

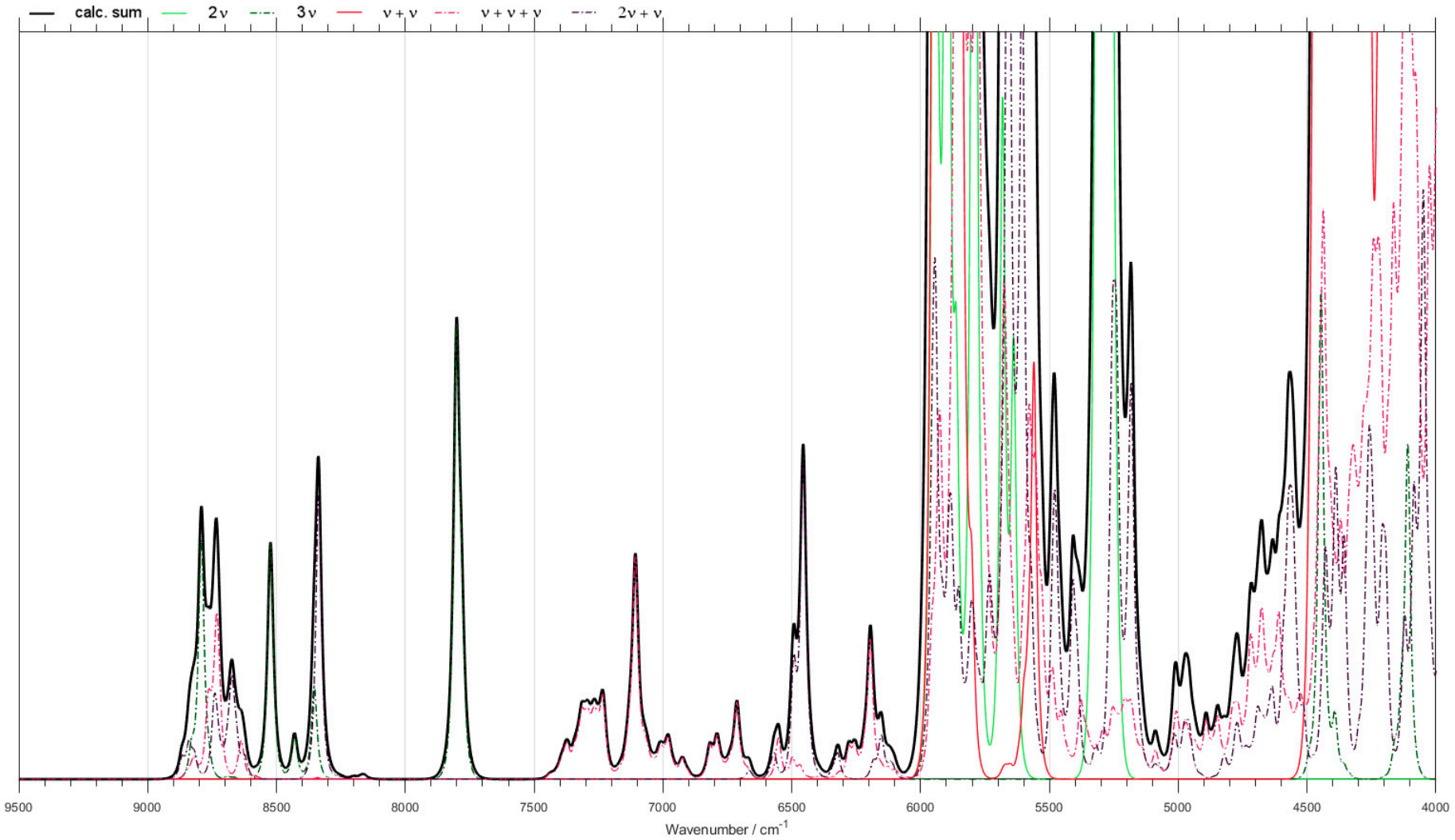

Figure S34. (High-resolution copy of Figure 4) Contributions from minor bands in NIR spectra of CH_3CH_2OD calculated with GVPT2 method at B2PLYP-GD3BJ/def2-TZVP//CPCM level of electronic theory.

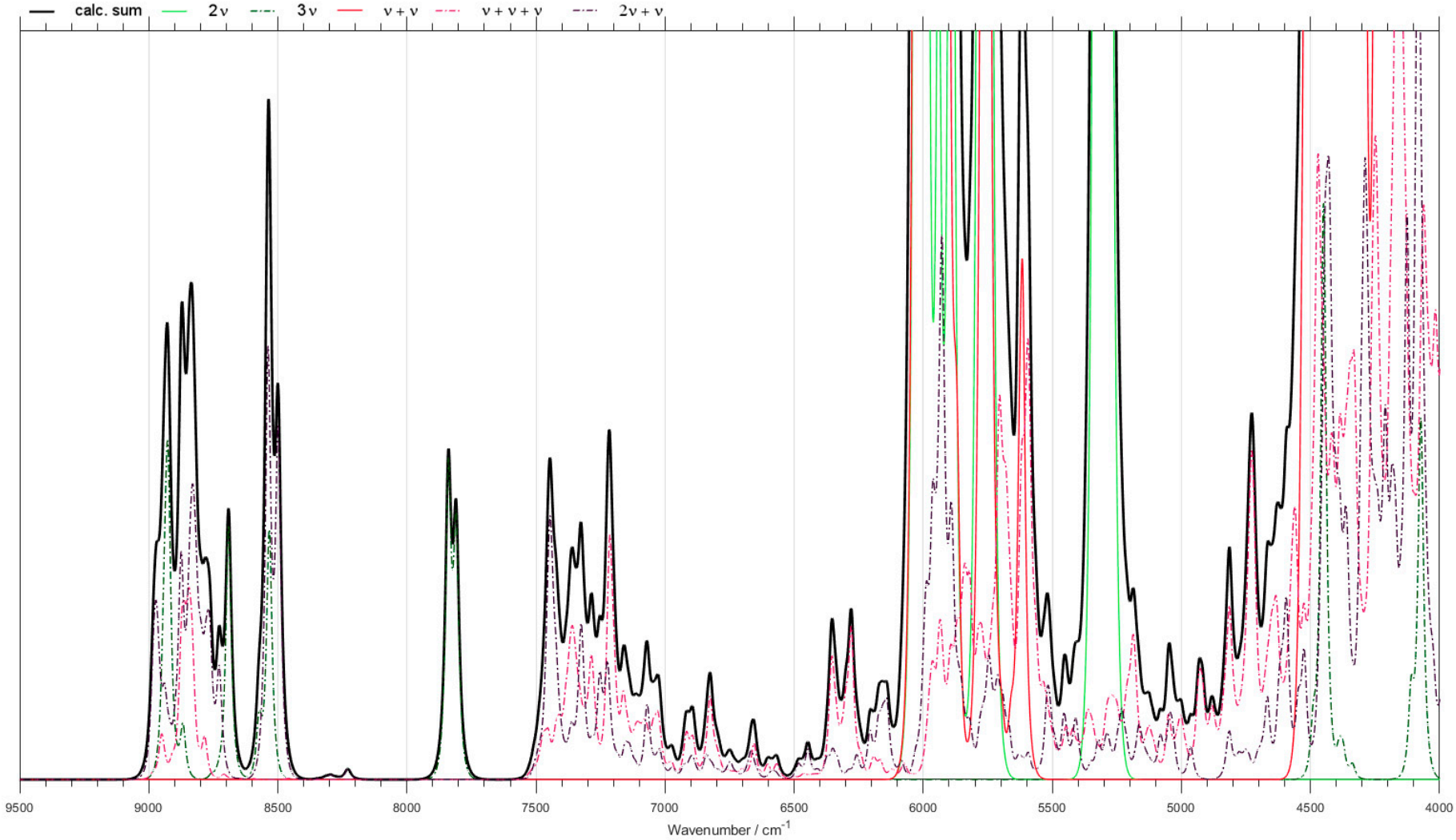

Figure S35. (High-resolution copy of Figure 4) Contributions from minor bands in NIR spectra of CH_3CH_2OD calculated with GVPT2 method at MP2/aug-cc-pVTZ//CPCM level of electronic theory.

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II. Tables

Table S1. The relative abundances of gauche (g) and trans (t) conformers for ethanol isotopomers calculated by different methods.

	Conf.	Calculated abundance						
		MP2 /aVTZ +CPCM	B2PLYP-GD3BJ /def2-TZVP +CPCM	B2PLYP-GD3BJ /SNST +CPCM	MP2 /6-31G(d,p) +CPCM	B2PLYP-GD3BJ /6-31G(d,p) +CPCM	B3LYP-GD3BJ /6-31G(d,p) +CPCM	B3LYP-GD3BJ /6-31G(d,p)
CH_3CH_2OH	*g*	45%	37%	82%	40%	87%	74%	79%
	t	55%	63%	18%	60%	13%	26%	21%
CH_3CH_2OD	*g*	48%	24%	73%	46%	78%	76%	79%
	t	52%	76%	27%	54%	22%	24%	21%
CH_3CD_2OH	*g*	47%	38%	83%	44%	87%	74%	79%
	t	53%	62%	17%	56%	13%	26%	21%
CD_3CH_2OH	*g*	60%	51%	83%	52%	88%	73%	79%
	t	40%	49%	17%	48%	12%	27%	21%
CD_3CD_2OH	*g*	58%	51%	84%	54%	87%	73%	79%
	t	42%	49%	16%	46%	13%	27%	21%
CD_3CD_2OD	*g*	51%	37%	69%	53%	80%	77%	79%
	t	49%	63%	31%	47%	20%	23%	21%
CH_3CD_2OD	*g*	48%	24%	73%	46%	79%	76%	79%
	t	52%	76%	27%	54%	21%	24%	21%
CD_3CH_2OD	*g*	50%	35%	70%	52%	80%	77%	79%
	t	50%	65%	30%	48%	20%	23%	21%

Table S2. Potential energy distribution (PED) for *trans* and *gauche* conformers of ethanol (CH_3CH_2OH) based on B2PLYP-GD3BJ/def2-TZVP//CPCM calculations.

trans

ν [cm^{-1}]	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.
240.08	**53%**	τCC	**45%**	δ_{oop}COH						
282.43	**53%**	δ_{oop}COH	**42%**	τCC						
420.77	**78%**	$\delta_{sciss}CH_2CO$	**12%**	$\delta_{rock'}CH_3$						
826.43	**40%**	$\delta_{rock}CH_2$	**33%**	$\delta_{rock}CH_3$	**13%**	$\delta_{twist}CH_2$	**11%**	$\delta_{rock'}CH_3$		
904.94	**38%**	νC-O	**24%**	νCC	**21%**	$\delta_{rock'}CH_3$	**7%**	$\delta_{rock}CH_3$	**6%**	$\delta_{wagg}CH_2$
1045.00	**49%**	νCC	**21%**	δ_{ip}COH	**14%**	νC-O	**8%**	$\delta_{rock'}CH_3$		
1105.80	**54%**	νC-O	**22%**	$\delta_{rock'}CH_3$	**8%**	$\delta_{rock}CH_3$	**5%**	$\delta_{sciss}CH_2CO$		

1188.46	**55%**	$\delta_{rock}CH_2$	**21%**	$\delta_{rock}CH_3$	**11%**	$\delta_{twist}CH_2$	**7%**	$\delta_{rock'}CH_3$		
1272.73	**58%**	$\delta_{ip}COH$	**18%**	$\delta_{wagg}CH_2$	**7%**	$\delta_{rock'}CH_3$				
1310.73	**85%**	$\delta_{twist}CH_2$	**9%**	$\delta_{rock}CH_3$						
1414.01	**85%**	$\delta_{s}CH_3$	**10%**	$\delta_{wagg}CH_2$						
1462.36	**60%**	$\delta_{wagg}CH_2$	**14%**	$\delta_{ip}COH$	**12%**	νCC	**8%**	$\delta_{s}CH_3$		
1492.43	**68%**	$\delta_{as}CH_3$	**23%**	$\delta_{as'}CH_3$	**6%**	$\delta_{rock}CH_3$				
1508.12	**58%**	$\delta_{as'}CH_3$	**19%**	$\delta_{as}CH_3$	**10%**	$\delta_{sciss}CH_2$				
1541.60	**87%**	$\delta_{sciss}CH_2$								
3016.45	**100%**	$\nu_{s}CH_2$								
3047.82	**98%**	$\nu_{as}CH_2$								
3058.32	**99%**	$\nu_{s}CH_3$								
3132.50	**100%**	$\nu_{as}CH_3$								
3134.94	**98%**	$\nu_{as'}CH_3$								
3821.81	**100%**	νOH								

gauche

ν [cm^{-1}]	**%**	**Int. coord.**	**%**	**Int. coord.**	**%**	**Int. coord.**	**%**	**Int. coord.**	**%**	**Int. coord.**
267.71	**89%**	τCC	**8%**	$\delta_{oop}COH$						
292.31	**84%**	$\delta_{oop}COH$	**9%**	τCC						
425.65	**76%**	$\delta_{sciss}CH_2CO$	**14%**	$\delta_{rock'}CH_3$						
814.37	**44%**	$\delta_{rock}CH_2$	**31%**	$\delta_{rock}CH_3$	**11%**	$\delta_{twist}CH_2$	**9%**	$\delta_{rock'}CH_3$		
892.97	**33%**	νC-O	**30%**	νCC	**23%**	$\delta_{rock'}CH_3$	**6%**	$\delta_{rock}CH_3$		
1072.09	**33%**	$\delta_{ip}COH$	**25%**	$\delta_{rock}CH_3$	**9%**	$\delta_{rock}CH_2$	**8%**	νC-O	**7%**	$\delta_{rock'}CH_3$
	7%	$\delta_{twist}CH_2$								
1076.14	**52%**	νC-O	**45%**	νCC						
1142.84	**36%**	$\delta_{rock'}CH_3$	**21%**	$\delta_{rock}CH_2$	**12%**	νC-O	**9%**	$\delta_{sciss}CH_2CO$	**7%**	$\delta_{twist}CH_2$
1291.84	**38%**	$\delta_{twist}CH_2$	**22%**	$\delta_{ip}COH$	**18%**	$\delta_{rock}CH_3$	**12%**	$\delta_{rock}CH_2$		
1381.13	**37%**	$\delta_{twist}CH_2$	**28%**	$\delta_{ip}COH$	**22%**	$\delta_{wagg}CH_2$				
1412.78	**72%**	$\delta_{s}CH_3$	**17%**	$\delta_{wagg}CH_2$						
1429.26	**54%**	$\delta_{wagg}CH_2$	**21%**	$\delta_{s}CH_3$	**10%**	νCC	**6%**	$\delta_{ip}COH$		
1497.42	**62%**	$\delta_{as}CH_3$	**27%**	$\delta_{as'}CH_3$	**7%**	$\delta_{rock}CH_3$				
1501.59	**50%**	$\delta_{as'}CH_3$	**24%**	$\delta_{as}CH_3$	**17%**	$\delta_{sciss}CH_2$				
1530.40	**82%**	$\delta_{sciss}CH_2$	**9%**	$\delta_{as'}CH_3$						
3027.04	**99%**	$\nu_{s}CH_2$								
3046.71	**99%**	$\nu_{s}CH_3$								
3100.59	**57%**	$\nu_{as}CH_2$	**39%**	$\nu_{as}CH_3$						
3120.42	**69%**	$\nu_{as'}CH_3$	**28%**	$\nu_{as}CH_2$						
3132.07	**90%**	$\nu_{as}CH_3$	**8%**	$\nu_{as}CH_2$						
3808.92	**100%**	νOH								

Table S3. Potential energy distribution (PED) for *trans* and *gauche* conformers of ethanol-*d*$_1$ (CH_3CH_2OD) based on B2PLYP-GD3BJ/def2-TZVP//CPCM calculations.

trans

ν [cm^{-1}]	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.
190.45	**88%**	δ_{oop}COD	**11%**	τCC						
263.60	**91%**	τCC								
411.13	**77%**	$\delta_{sciss}CH_2CO$	**11%**	$\delta_{rock'}CH_3$						
826.34	**40%**	$\delta_{rock}CH_2$	**33%**	$\delta_{rock}CH_3$	**13%**	$\delta_{twist}CH_2$	**11%**	$\delta_{rock'}CH_3$		
863.78	**60%**	δ_{ip}COD	**32%**	νCC	**7%**	νC-O				
914.47	**30%**	νC-O	**25%**	$\delta_{rock'}CH_3$	**22%**	δ_{ip}COD	**9%**	$\delta_{wagg}CH_2$	**8%**	$\delta_{rock}CH_3$
1085.01	**55%**	νC-O	**39%**	νCC						
1167.15	**27%**	$\delta_{rock'}CH_3$	**15%**	δ_{ip}COD	**14%**	$\delta_{sciss}CH_2CO$	**14%**	νCC	**13%**	νC-O
	9%	$\delta_{rock}CH_3$								
1188.46	**55%**	$\delta_{rock}CH_2$	**21%**	$\delta_{rock}CH_3$	**11%**	$\delta_{twist}CH_2$	**7%**	$\delta_{rock'}CH_3$		
1310.71	**85%**	$\delta_{twist}CH_2$	**9%**	$\delta_{rock}CH_3$						
1412.18	**73%**	δ_sCH_3	**23%**	$\delta_{wagg}CH_2$						
1441.73	**60%**	$\delta_{wagg}CH_2$	**19%**	δ_sCH_3	**13%**	νCC				
1492.41	**68%**	$\delta_{as}CH_3$	**23%**	$\delta_{as'}CH_3$	**6%**	$\delta_{rock}CH_3$				
1507.94	**59%**	$\delta_{as}'CH_3$	**19%**	$\delta_{as}CH_3$	**10%**	$\delta_{sciss}CH_2$				
1541.60	**87%**	$\delta_{sciss}CH_2$								
2782.51	**100%**	νOD								
3016.41	**100%**	ν_sCH_2								
3047.82	**98%**	$\nu_{as}CH_2$								
3058.32	**99%**	ν_sCH_3								
3132.50	**100%**	$\nu_{as}CH_3$								
3134.94	**98%**	$\nu_{as'}CH_3$								

gauche

ν [cm^{-1}]	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.
214.16	**94%**	δ_{oop}COD										
269.87	**90%**	τCC										
418.35	**76%**	$\delta_{sciss}CH_2CO$	**14%**	$\delta_{rock'}CH_3$								
802.16	**46%**	$\delta_{rock}CH_2$	**21%**	$\delta_{rock}CH_3$	**11%**	δ_{ip}COD	**11%**	$\delta_{rock'}CH_3$	**7%**	$\delta_{twist}CH_2$		
890.32	**23%**	νC-O	**22%**	$\delta_{rock}CH_3$	**18%**	νCC	**17%**	$\delta_{rock'}CH_3$	**11%**	δ_{ip}COD	**6%**	$\delta_{wagg}CH_2$
898.75	**52%**	δ_{ip}COD	**13%**	νCC	**11%**	νC-O	**9%**	$\delta_{twist}CH_2$	**8%**	$\delta_{rock}CH_3$	**5%**	$\delta_{rock'}CH_3$
1075.02	**54%**	νC-O	**42%**	νCC								
1129.02	**44%**	$\delta_{rock'}CH_3$	**16%**	νC-O	**15%**	$\delta_{sciss}CH_2CO$	**10%**	νCC				
1227.78	**46%**	$\delta_{rock}CH_2$	**30%**	$\delta_{rock}CH_3$	**13%**	δ_{ip}COD						
1336.60	**90%**	$\delta_{twist}CH_2$										
1408.02	**49%**	$\delta_{wagg}CH_2$	**47%**	dsCH3								

1424.48	**42%**	dsCH3	**40%**	$\delta_{wagg}CH_2$	**11%**	νCC						
1496.19	**61%**	$\delta_{as}CH_3$	**29%**	$\delta_{as'}CH_3$	**7%**	$\delta_{rock}CH_3$						
1501.56	**48%**	$\delta_{as'}CH_3$	**26%**	$\delta_{as}CH_3$	**16%**	$\delta_{sciss}CH_2$						
1530.30	**82%**	$\delta_{sciss}CH_2$	**9%**	$\delta_{as'}CH_3$								
2772.31	**100%**	νOD										
3027.09	**99%**	$\nu_s CH_2$										
3046.76	**99%**	$\nu_s CH_3$										
3100.95	**56%**	$\nu_{as} CH_2$	**41%**	$\nu_{as} CH_3$								
3120.52	**69%**	$\nu_{as'} CH_3$	**29%**	$\nu_{as} CH_2$								
3132.08	**90%**	$\nu_{as} CH_3$	**8%**	$\nu_{as} CH_2$								

Table S4. Potential energy distribution (PED) for *trans* and *gauche* conformers of ethanol-d_2 (CH_3CD_2OH) based on B2PLYP-GD3BJ/def2-TZVP//CPCM calculations.

trans

ν [cm^{-1}]	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.
238.36	**57%**	τCC	**41%**	δ_{oop} COH						
279.21	**59%**	δ_{oop} COH	**37%**	τCC						
415.53	**78%**	$\delta_{sciss}CD_2CO$	**11%**	$\delta_{rock'}CH_3$						
692.46	**48%**	$\delta_{rock}CD_2$	**23%**	δ_{twist} CD_2	**20%**	$\delta_{rock}CH_3$	**7%**	$\delta_{rock'}CH_3$		
868.09	**31%**	νCC	**26%**	$\delta_{wagg}CD_2$	**17%**	νC-O	**16%**	$\delta_{rock'}CH_3$	**6%**	$\delta_{rock}CH_3$
929.51	**71%**	δ_{twist} CD_2	**26%**	$\delta_{rock}CD_2$						
976.18	**66%**	νC-O	**30%**	$\delta_{wagg}CD_2$						
1024.92	**26%**	νCC	**18%**	$\delta_{rock'}CH_3$	**16%**	δ_{ip} COH	**16%**	$\delta_{sciss}CD_2$	**6%**	$\delta_{sciss}CD_2CO$
	6%	$\delta_{rock}CH_3$	**6%**	νC-O						
1130.99	**60%**	$\delta_{sciss}CD_2$	**15%**	νCC	**13%**	δ_{ip} COH	**7%**	$\delta_{wagg}CD_2$		
1152.61	**50%**	$\delta_{rock}CH_3$	**17%**	$\delta_{rock}CD_2$	**16%**	$\delta_{rock'}CH_3$	**9%**	δ_{twist} CD_2	**6%**	dasCH3
1191.98	**28%**	νC-O	**23%**	$\delta_{wagg}CD_2$	**18%**	$\delta_{rock'}CH_3$	**15%**	$\delta_{sciss}CD_2$	**6%**	$\delta_{rock}CH_3$
1339.86	**61%**	δ_{ip}COH	**15%**	$\delta_{wagg}CD_2$	**11%**	νCC	**8%**	dsCH3		
1423.43	**83%**	$\delta_s CH_3$	**12%**	νCC						
1491.00	**69%**	$\delta_{as}CH_3$	**23%**	$\delta_{as'}CH_3$	**6%**	$\delta_{rock}CH_3$				
1509.03	**68%**	$\delta_{as'}CH_3$	**22%**	$\delta_{as}CH_3$	**6%**	$\delta_{rock'}CH_3$				
2192.04	**99%**	$\nu_s CD_2$								
2266.52	**98%**	$\nu_{as} CD_2$								
3058.29	**100%**	$\nu_s CH_3$								
3132.15	**100%**	$\nu_{as} CH_3$								
3133.16	**100%**	$\nu_{as'} CH_3$								
3821.79	**100%**	νOH								

gauche

ν [cm^{-1}]	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.
264.47	**94%**	τCC								

289.31	**91%**	$\delta_{oop}COH$								
420.04	**76%**	$\delta_{sciss}CD_2CO$	**13%**	$\delta_{rock'}CH_3$						
683.50	**53%**	$\delta_{rock}CD_2$	**19%**	$\delta_{rock}CH_3$	**18%**	$\delta_{twist}CD_2$	**6%**	$\delta_{rock'}CH_3$		
858.34	**37%**	νCC	**22%**	$\delta_{wagg}CD_2$	**17%**	$\delta_{rock'}CH_3$	**15%**	νC-O		
904.18	**62%**	$\delta_{ip}COH$	**17%**	$\delta_{rock}CD_2$	**14%**	$\delta_{ip}COH$				
979.09	**67%**	νC-O	**24%**	$\delta_{wagg}CD_2$						
1047.93	**38%**	$\delta_{sciss}CD_2$	**21%**	$\delta_{rock'}CH_3$	**14%**	νCC	**10%**	$\delta_{sciss}CD_2CO$	**10%**	$\delta_{rock}CH_3$
1137.78	**41%**	$\delta_{rock}CH_3$	**22%**	$\delta_{sciss}CD_2$	**13%**	$\delta_{ip}COH$	**7%**	$\delta_{ip}COH$	**5%**	$\delta_{rock}CD_2$
1155.43	**45%**	$\delta_{sciss}CD_2$	**18%**	νCC	**16%**	$\delta_{rock'}CH_3$	**6%**	$\delta_{rock}CD_2$		
1193.50	**43%**	$\delta_{wagg}CD_2$	**28%**	νC-O	**13%**	νCC	**10%**	$\delta_{rock'}CH_3$		
1322.11	**83%**	$\delta_{ip}COH$								
1417.05	**90%**	$\delta_{s}CH_3$	**8%**	νCC						
1495.37	**71%**	$\delta_{as}CH_3$	**20%**	$\delta_{as'}CH_3$	**6%**	$\delta_{rock}CH_3$				
1504.32	**70%**	$\delta_{as'}CH_3$	**21%**	$\delta_{as}CH_3$	**5%**	$\delta_{rock'}CH_3$				
2208.01	**98%**	$\nu_{s}CD_2$								
2305.19	**98%**	$\nu_{as}CD_2$								
3046.67	**99%**	$\nu_{s}CH_3$								
3113.45	**95%**	$\nu_{as'}CH_3$								
3129.50	**96%**	$\nu_{as}CH_3$								
3808.77	**100%**	νOH								

Table S5. Potential energy distribution (PED) for *trans* and *gauche* conformers of ethanol-d_3 (CD_3CH_2OH) based on B2PLYP-GD3BJ/def2-TZVP//CPCM calculations.

trans

ν [cm^{-1}]	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.
192.63	**85%**	τCC	**10%**	δ_{oop}COH						
266.42	**95%**	δ_{oop}COH								
376.32	**70%**	$\delta_{sciss}CH_2CO$	**18%**	$\delta_{rock'}CD_3$	**6%**	$\delta_{rock}CD_3$				
683.12	**48%**	$\delta_{rock}CD_3$	**23%**	$\delta_{rock}CH_2$	**16%**	$\delta_{rock'}CD_3$	**9%**	$\delta_{twist}CH_2$		
770.55	**40%**	$\delta_{rock'}CD_3$	**19%**	νC-O	**14%**	νCC	**14%**	$\delta_{rock}CD_3$		
934.38	**34%**	νCC	**31%**	$\delta_s CD_3$	**10%**	$\delta_{sciss}CH_2CO$	**10%**	δ_{ip}COH	**9%**	$\delta_{rock'}CD_3$
1061.99	**63%**	νC-O	**17%**	$\delta_{as'}CD_3$	**6%**	$\delta_{sciss}CH_2CO$	**6%**	$\delta_{as}CD_3$		
1072.32	**72%**	$\delta_{as}CD_3$	**24%**	$\delta_{as'}CD_3$						
1090.74	**54%**	$\delta_{as'}CD_3$	**18%**	$\delta_{as}CD_3$	**16%**	νC-O	**5%**	$\delta_{rock'}CD_3$		
1125.48	**79%**	$\delta_{rock}CH_2$	**15%**	$\delta_{rock}CD_3$						
1154.80	**48%**	$\delta_s CD_3$	**33%**	νCC	**11%**	δ_{ip}COH	**6%**	νC-O		
1257.45	**59%**	δ_{ip}COH	**25%**	$\delta_{twist}CH_2$	**6%**	νCC				
1284.71	**96%**	$\delta_{twist}CH_2$								
1459.15	**72%**	$\delta_{wagg}CH_2$	**15%**	δ_{ip}COH	**10%**	νCC				
1538.68	**95%**	$\delta_{sciss}CH_2$								
2197.73	**99%**	$\nu_s CD_3$								
2320.27	**98%**	$\nu_{as}CD_3$								
2322.02	**98%**	$\nu_{as'}CD_3$								
3016.88	**100%**	$\nu_s CH_2$								
3049.95	**100%**	$\nu_{as}CH_2$								
3821.81	**100%**	νOH								

gauche

ν [cm^{-1}]	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.
204.58	**94%**	τCC								
287.82	**89%**	δ_{oop}COH								
382.13	**66%**	$\delta_{sciss}CH_2CO$	**21%**	$\delta_{rock'}CD_3$						
677.65	**49%**	$\delta_{rock}CD_3$	**25%**	$\delta_{rock}CH_2$	**13%**	$\delta_{rock'}CD_3$	**9%**	$\delta_{twist}CH_2$		
761.11	**40%**	$\delta_{rock'}CD_3$	**20%**	νCC	**16%**	νC-O	**12%**	$\delta_{rock}CD_3$	**6%**	$\delta_s CD_3$
950.19	**33%**	$\delta_s CD_3$	**28%**	νCC	**13%**	$\delta_{sciss}CH_2CO$	**11%**	$\delta_{rock'}CD_3$	**6%**	$\delta_{rock}CD_3$
	6%	δ_{ip}COH								
1038.09	**42%**	νC-O	**21%**	δ_{ip}COH	**20%**	$\delta_{rock}CH_2$	**6%**	$\delta_{rock}CD_3$	**6%**	$\delta_s CD_3$
1073.56	**78%**	$\delta_{as}CD_3$	**11%**	$\delta_{rock}CH_2$	**7%**	νC-O				
1076.18	**69%**	$\delta_{as'}CD_3$	**9%**	$\delta_{rock}CH_2$	**7%**	νC-O	**5%**	$\delta_{rock}CD_3$		
1092.43	**28%**	νC-O	**25%**	$\delta_{as'}CD_3$	**15%**	$\delta_{as}CD_3$	**14%**	$\delta_{rock}CH_2$	**13%**	$\delta_{rock'}CD_3$
1163.57	**50%**	$\delta_s CD_3$	**44%**	νCC						
1247.02	**55%**	$\delta_{twist}CH_2$	**30%**	δ_{ip}COH	**7%**	$\delta_{rock}CH_2$	**5%**	$\delta_{rock'}CD_3$		
1378.71	**33%**	$\delta_{twist}CH_2$	**29%**	δ_{ip}COH	**27%**	$\delta_{wagg}CH_2$	**5%**	$\delta_{rock}CH_2$		

1425.30	**73%**	$\delta_{wagg}CH_2$	**13%**	$\delta_{ip}COH$	**6%**	νCC				
1526.06	**95%**	$\delta_{sciss}CH_2$								
2189.67	**98%**	ν_sCD_3								
2306.01	**96%**	$\nu_{as'}CD_3$								
2318.96	**99%**	$\nu_{as}CD_3$								
3027.99	**99%**	ν_sCH_2								
3109.63	**100%**	$\nu_{as}CH_2$								
3808.90	**100%**	νOH								

Table S6. Potential energy distribution (PED) for *trans* and *gauche* conformers of ethanol-d_5 (CD_3CD_2OH) based on B2PLYP-GD3BJ/def2-TZVP//CPCM calculations.

trans

ν [cm^{-1}]	**%**	**Int. coord.**	**%**	**Int. coord.**	**%**	**Int. coord.**	**%**	**Int. coord.**	**%**	**Int. coord.**
187.52	**87%**	τCC	**9%**	$\delta_{oop}COH$						
265.38	**96%**	$\delta_{oop}COH$								
372.06	**70%**	$\delta_{sciss}CD_2CO$	**17%**	$\delta_{rock'}CD_3$	**6%**	$\delta_{rock}CD_3$				
601.73	**35%**	$\delta_{rock}CD_2$	**35%**	$\delta_{rock}CD_3$	**16%**	$\delta_{twist}CD_2$	**11%**	$\delta_{rock'}CD_3$		
753.55	**34%**	$\delta_{rock'}CD_3$	**18%**	νCC	**14%**	νC-O	**13%**	$\delta_{wagg}CD_2$	**12%**	$\delta_{rock}CD_3$
	5%	δ_sCD_3								
903.34	**28%**	νCC	**19%**	δ_sCD_3	**15%**	$\delta_{rock'}CD_3$	**12%**	$\delta_{sciss}CD_2CO$	**8%**	$\delta_{sciss}CD_2$
	6%	$\delta_{ip}COH$	**5%**	$\delta_{rock}CD_3$						
928.30	**71%**	$\delta_{twist}CD_2$	**25%**	$\delta_{rock}CD_2$						
976.91	**52%**	νC-O	**33%**	$\delta_{wagg}CD_2$	**6%**	$\delta_{sciss}CD_2CO$				
1005.34	**38%**	$\delta_{rock}CD_2$	**33%**	$\delta_{rock}CD_3$	**17%**	$\delta_{twist}CD_2$	**11%**	$\delta_{rock'}CD_3$		
1074.89	**72%**	$\delta_{as}CD_3$	**24%**	$\delta_{as'}CD_3$						
1083.27	**66%**	$\delta_{as'}CD_3$	**22%**	$\delta_{as}CD_3$	**6%**	$\delta_{sciss}CD_2$				
1091.17	**27%**	δ_sCD_3	**25%**	$\delta_{wagg}CD_2$	**18%**	$\delta_{sciss}CD_2$	**14%**	νC-O		
1154.70	**53%**	$\delta_{sciss}CD_2$	**16%**	δ_sCD_3	**15%**	νCC	**6%**	νC-O	**5%**	$\delta_{ip}COH$
1163.43	**23%**	νC-O	**17%**	δ_sCD_3	**16%**	$\delta_{ip}COH$	**16%**	νCC	**14%**	$\delta_{wagg}CD_2$
	8%	$\delta_{sciss}CD_2$								
1348.97	**55%**	$\delta_{ip}COH$	**21%**	νCC	**17%**	$\delta_{wagg}CD_2$				
2189.80	**80%**	ν_sCD_2	**20%**	ν_sCD_3						
2199.60	**79%**	ν_sCD_3	**18%**	ν_sCD_2						
2265.09	**96%**	$\nu_{as}CD_2$								
2320.38	**98%**	$\nu_{as}CD_3$								
2323.35	**96%**	$\nu_{as'}CD_3$								
3821.79	**100%**	νOH								

gauche

ν [cm^{-1}]	**%**	**Int. coord.**	**%**	**Int. coord.**	**%**	**Int. coord.**	**%**	**Int. coord.**	**%**	**Int. coord.**
198.93	**96%**	τCC								

286.11	**91%**	δ_{oop}COH								
377.64	**66%**	$\delta_{sciss}CD_2CO$	**20%**	$\delta_{rock'}CD_3$						
595.93	**38%**	$\delta_{rock}CD_2$	**35%**	$\delta_{rock}CD_3$	**15%**	$\delta_{twist}CD_2$	**10%**	$\delta_{rock'}CD_3$		
744.86	**34%**	$\delta_{rock'}CD_3$	**24%**	νCC	**11%**	νC-O	**11%**	dwaggCH2	**11%**	$\delta_{rock}CD_3$
	6%	δ_sCD_3								
894.42	**38%**	$\delta_{twist}CD_2$	**24%**	$\delta_{rock}CD_2$	**15%**	δ_{ip}COH	**9%**	$\delta_{rock}CD_3$		
918.78	**17%**	νCC	**16%**	$\delta_{rock'}CD_3$	**14%**	δ_sCD_3	**11%**	$\delta_{twist}CD_2$	**11%**	$\delta_{sciss}CD_2CO$
	8%	$\delta_{sciss}CD_2$	**7%**	νC-O	**6%**	$\delta_{rock}CD_2$	**5%**	$d\delta_{wagg}CD_2$		
981.92	**48%**	νC-O	**18%**	$\delta_{wagg}CD_2$	**12%**	$\delta_{twist}CD_2$	**7%**	$\delta_{sciss}CD_2CO$		
1000.98	**29%**	$\delta_{twist}CD_2$	**25%**	$\delta_{rock}CD_3$	**22%**	$\delta_{rock}CD_2$	**12%**	$\delta_{rock'}CD_3$	**5%**	νC-O
1076.06	**65%**	$\delta_{as}CD_3$	**31%**	$\delta_{as'}CD_3$						
1080.46	**58%**	$\delta_{as'}CD_3$	**29%**	$\delta_{as}CD_3$	**7%**	$\delta_{sciss}CD_2$				
1097.28	**42%**	δ_sCD_3	**23%**	$\delta_{wagg}CD_2$	**18%**	$\delta_{sciss}CD_2$	**7%**	νC-O	**6%**	$\delta_{as'}CD_3$
1143.62	**57%**	$\delta_{sciss}CD_2$	**19%**	νC-O	**7%**	$\delta_{wagg}CD_2$	**5%**	$\delta_{rock'}CD_3$		
1206.44	**39%**	νCC	**28%**	$\delta_{wagg}CD_2$	**16%**	δ_sCD_3	**14%**	νC-O		
1319.55	**86%**	δ_{ip}COH								
2189.05	**96%**	ν_sCD_3								
2208.19	**95%**	ν_sCD_2								
2298.37	**55%**	$\nu_{as}CD_2$	**42%**	$\nu_{as}CD_3$						
2310.52	**67%**	$\nu_{as'}CD_3$	**29%**	$\nu_{as}CD_2$						
2321.35	**86%**	$\nu_{as}CD_3$	**9%**	$\nu_{as}CD_2$						
3808.76	**100%**	νOH								

Table S7. Potential energy distribution (PED) for *trans* and *gauche* conformers of ethanol-d_6 (CD_3CD_2OD) based on B2PLYP-GD3BJ/def2-TZVP//CPCM calculations.

trans

ν [cm^{-1}]	**%**	**Int. coord.**	**%**	**Int. coord.**	**%**	**Int. coord.**	**%**	**Int. coord.**	**%**	**Int. coord.**
179.69	**53%**	τCC	**45%**	δ_{oop}COD						
204.12	**52%**	δ_{oop}COD	**44%**	τCC						
364.00	**70%**	$\delta_{sciss}CD_2CO$	**17%**	$\delta_{rock'}CD_3$	**6%**	$\delta_{rock}CD_3$				
601.58	**35%**	$\delta_{rock}CD_2$	**35%**	$\delta_{rock}CD_3$	**16%**	$\delta_{twist}CD_2$	**11%**	$\delta_{rock'}CD_3$		
751.58	**35%**	$\delta_{rock'}CD_3$	**15%**	νCC	**14%**	$\delta_{wagg}CD_2$	**13%**	νC-O	**12%**	$\delta_{rock}CD_3$
828.13	**56%**	δ_{ip}COD	**21%**	νCC	**7%**	δ_sCD_3				
928.30	**71%**	$\delta_{twist}CD_2$	**25%**	$\delta_{rock}CD_2$						
929.81	**27%**	νC-O	**27%**	$\delta_{wagg}CD_2$	**11%**	δ_sCD_3	**10%**	νCC	**8%**	$\delta_{rock'}CD_3$
	5%	δ_{ip}COD								
1005.34	**38%**	$\delta_{rock}CD_2$	**33%**	$\delta_{rock}CD_3$	**17%**	$\delta_{twist}CD_2$	**11%**	$\delta_{rock'}CD_3$		
1040.69	**37%**	νC-O	**22%**	δ_{ip}COD	**19%**	$\delta_{sciss}CD_2$	**12%**	$\delta_{sciss}CD_2CO$		
1074.86	**72%**	$\delta_{as}CD_3$	**24%**	$\delta_{as'}CD_3$						
1083.27	**67%**	$\delta_{as'}CD_3$	**22%**	$\delta_{as}CD_3$	**6%**	$\delta_{sciss}CD_2$				
1104.25	**60%**	δ_sCD_3	**21%**	$\delta_{wagg}CD_2$	**5%**	$\delta_{sciss}CD_2$				

1157.79	**55%**	$\delta_{sciss}CD_2$	**24%**	νC-O	**10%**	$\delta_{wagg}CD_2$	**5%**	$\delta_{rock'}CD_3$		
1256.52	**44%**	νCC	**28%**	$\delta_{wagg}CD_2$	**11%**	δ_sCD_3	**7%**	$\delta_{ip}COD$		
2189.63	**80%**	ν_sCD_2	**17%**	ν_sCD_3						
2199.52	**79%**	ν_sCD_3	**18%**	ν_sCD_2						
2265.08	**96%**	$\nu_{as}CD_2$								
2320.37	**98%**	$\nu_{as}CD_3$								
2323.35	**96%**	$\nu_{as'}CD_3$								
2782.50	**100%**	νOD								

gauche

ν [cm^{-1}]	**%**	**Int. coord.**	**%**	**Int. coord.**	**%**	**Int. coord.**	**%**	**Int. coord.**	**%**	**Int. coord.**
193.34	**79%**	τCC	**18%**	$\delta_{oop}COD$						
215.82	**73%**	$\delta_{oop}COD$	**20%**	τCC						
371.21	**68%**	$\delta_{sciss}CD_2CO$	**20%**	$\delta_{rock'}CD_3$						
593.24	**39%**	$\delta_{rock}CD_2$	**32%**	$\delta_{rock}CD_3$	**14%**	$\delta_{twist}CD_2$	**11%**	$\delta_{rock'}CD_3$		
739.08	**32%**	$\delta_{rock'}CD_3$	**19%**	νCC	**17%**	$\delta_{rock}CD_3$	**11%**	$\delta_{wagg}CD_2$	**10%**	νC-O
812.42	**47%**	$\delta_{ip}COD$	**21%**	$\delta_{twist}CD_2$	**12%**	$\delta_{rock}CD_2$	**8%**	νCC	**6%**	$\delta_{rock}CD_3$
918.23	**19%**	νCC	**17%**	$\delta_{rock'}CD_3$	**15%**	δ_sCD_3	**11%**	$\delta_{sciss}CD_2CO$	**9%**	$\delta_{sciss}CD_2$
	8%	$\delta_{twist}CD_2$	**7%**	νC-O	**6%**	$\delta_{wagg}CD_2$				
980.31	**44%**	νC-O	**19%**	$\delta_{twist}CD_2$	**17%**	$\delta_{wagg}CD_2$	**6%**	$\delta_{sciss}CD_2CO$	**5%**	$\delta_{rock}CD_3$
995.22	**40%**	$\delta_{twist}CD_2$	**15%**	$\delta_{rock}CD_3$	**13%**	$\delta_{rock'}CD_3$	**9%**	$\delta_{rock}CD_2$	**8%**	νC-O
1064.16	**33%**	$\delta_{as}CD_3$	**22%**	$\delta_{ip}COD$	**20%**	$\delta_{rock}CD_2$	**13%**	$\delta_{sciss}CD_2$		
1078.79	**75%**	$\delta_{as'}CD_3$	**10%**	$\delta_{sciss}CD_2$	**5%**	δ_sCD_3				
1084.38	**62%**	$\delta_{as}CD_3$	**12%**	$\delta_{as'}CD_3$	**7%**	$\delta_{ip}COD$				
1102.03	**47%**	δ_sCD_3	**21%**	$\delta_{wagg}CD_2$	**8%**	nC-O	**7%**	$\delta_{ip}COD$		
1154.46	**56%**	$\delta_{sciss}CD_2$	**22%**	νC-O	**9%**	$\delta_{wagg}CD_2$				
1211.74	**41%**	νCC	**26%**	$\delta_{wagg}CD_2$	**15%**	δ_sCD_3	**11%**	νC-O		
2189.05	**96%**	ν_sCD_3								
2208.15	**94%**	ν_sCD_2								
2298.13	**56%**	$\nu_{as}CD_2$	**40%**	$\nu_{as}CD_3$						
2310.31	**69%**	$\nu_{as'}CD_3$	**28%**	$\nu_{as}CD_2$						
2321.26	**86%**	$\nu_{as}CD_3$	**9%**	$\nu_{as}CD_2$						
2772.85	**100%**	νOD								

Table S8. Potential energy distribution (PED) for *trans* and *gauche* conformers of CH_3CD_2OD based on B2PLYP-GD3BJ/def2-TZVP//CPCM calculations.

trans

ν [cm^{-1}]	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.
190.00	**89%**	δ_{oop}COD	**11%**	τCC						
258.77	**92%**	τCC								
406.06	**77%**	$\delta_{sciss}CD_2CO$	**11%**	$\delta_{rock'}CH_3$						
692.37	**48%**	$\delta_{rock}CD_2$	**23%**	$\delta_{twist}CD_2$	**20%**	$\delta_{rock}CH_3$	**7%**	$\delta_{rock'}CH_3$		
852.44	**68%**	δ_{ip}COD	**14%**	$\delta_{wagg}CD_2$	**10%**	νCC				
867.18	**30%**	νCC	**26%**	$\delta_{wagg}CD_2$	**18%**	νC-O	**16%**	$\delta_{rock'}CH_3$	**6%**	$\delta_{rock}CH_3$
929.51	**71%**	$\delta_{twist}CD_2$	**26%**	$\delta_{rock}CD_2$						
988.62	**61%**	νC-O	**12%**	νCC	**10%**	δ_{ip}COD	**9%**	$\delta_{wagg}CD_2$	**5%**	$\delta_{rock'}CH_3$
1083.26	**61%**	$\delta_{sciss}CD_2$	**13%**	$\delta_{rock'}CH_3$	**11%**	$\delta_{sciss}CD_2CO$	**7%**	δ_{ip}COD		
1152.60	**50%**	$\delta_{rock}CH_3$	**17%**	$\delta_{rock}CD_2$	**16%**	$\delta_{rock'}CH_3$	**9%**	$\delta_{twist}CD_2$	**6%**	$\delta_{as}CH_3$
1187.81	**32%**	$\delta_{sciss}CD_2$	**23%**	νC-O	**19%**	$\delta_{rock'}CH_3$	**10%**	$\delta_{wagg}CD_2$	**7%**	$\delta_{rock}CH_3$
1233.96	**42%**	$\delta_{wagg}CD_2$	**33%**	νCC	**10%**	δ_{ip}COD	**7%**	νC-O	**5%**	$\delta_{sciss}CD_2$
1420.81	**88%**	δ_sCH_3	**10%**	νCC						
1490.98	**69%**	$\delta_{as}CH_3$	**23%**	$\delta_{as'}CH_3$	**6%**	$\delta_{rock}CH_3$				
1508.99	**68%**	$\delta_{as'}CH_3$	**22%**	$\delta_{as}CH_3$	**6%**	$\delta_{rock'}CH_3$				
2191.79	**98%**	ν_sCD_2								
2266.51	**98%**	$\nu_{as}CD_2$								
2782.50	**100%**	νOD								
3058.30	**100%**	ν_sCH_3								
3132.15	**100%**	$\nu_{as}CH_3$								
3133.16	**100%**	$\nu_{as'}CH_3$								

gauche

ν [cm^{-1}]	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.
212.69	**96%**	δ_{oop}COD								
264.92	**93%**	τCC								
412.62	**76%**	$\delta_{sciss}CD_22CO$	**13%**	$\delta_{rock'}CH_3$						
675.84	**56%**	$\delta_{rock}CD_2$	**16%**	$\delta_{rock}CH_3$	**14%**	$\delta_{twist}CD_2$	**7%**	$\delta_{rock'}CH_3$		
828.91	**44%**	δ_{ip}COD	**38%**	$\delta_{twist}CD_2$	**11%**	$\delta_{rock}CH_3$				
858.49	**37%**	νCC	**20%**	$\delta_{wagg}CD_2$	**17%**	$\delta_{rock'}CH_3$	**16%**	νC-O		
976.66	**69%**	νC-O	**25%**	$\delta_{wagg}CD_2$						
1021.81	**28%**	$\delta_{twist}CD_2$	**22%**	δ_{ip}COD	**12%**	νCC	**9%**	$\delta_{rock'}CH_3$	**9%**	$\delta_{rock}CH_3$
	8%	$\delta_{rock}CD_2$	**7%**	$\delta_{sciss}CD_2$						
1068.48	**49%**	$\delta_{sciss}CD_2$	**14%**	$\delta_{rock'}CH_3$	**12%**	δ_{ip}COD	**9%**	$\delta_{twist}CD_2$	**8%**	$\delta_{sciss}CD_2CO$
1151.99	**30%**	$\delta_{rock}CH_3$	**19%**	$\delta_{rock'}CH_3$	**15%**	$\delta_{sciss}CD_2$	**14%**	$\delta_{rock}CD_2$	**7%**	νCC
	5%	$\delta_{twist}CD_2$	**5%**	$\delta_{as}CH_3$						

1183.07	**37%**	$\delta_{sciss}CD_2$	**18%**	$\delta_{rock}CH_3$	**18%**	νCC	**10%**	δ_{ip}COD		
1193.39	**43%**	$\delta_{wagg}CD_2$	**28%**	νC-O	**13%**	νCC	**10%**	$\delta_{rock'}CH_3$		
1417.04	**90%**	δ_sCH_3	**8%**	νCC						
1494.71	**68%**	$\delta_{as}CH_3$	**23%**	$\delta_{as'}CH_3$	**6%**	$\delta_{rock}CH_3$				
1504.11	**67%**	$\delta_{as'}CH_3$	**24%**	$\delta_{as}CH_3$	**5%**	$\delta_{rock'}CH_3$				
2207.97	**98%**	ν_sCD_2								
2304.66	**97%**	$\nu_{as}CD_2$								
2772.81	**100%**	νOD								
3046.70	**99%**	ν_sCH_3								
3113.44	**95%**	$\nu_{as'}CH_3$								
3129.51	**96%**	$\nu_{as}CH_3$								

Table S9. Potential energy distribution (PED) for *trans* and *gauche* conformers of CD_3CH_2OD based on B2PLYP-GD3BJ/def2-TZVP//CPCM calculations.

trans

ν [cm^{-1}]	**%**	**Int. coord.**	**%**	**Int. coord.**	**%**	**Int. coord.**	**%**	**Int. coord.**	**%**	**Int. coord.**
181.66	**54%**	δ_{oop}COD	**44%**	τCC						
208.61	**54%**	τCC	**39%**	δ_{oop}COD						
368.12	**70%**	$\delta_{sciss}CH_2CO$	**17%**	$\delta_{rock'}CD_3$	**6%**	$\delta_{rock}CD_3$				
682.97	**48%**	$\delta_{rock}CD_3$	**23%**	$\delta_{rock}CH_2$	**16%**	$\delta_{rock'}CD_3$	**10%**	$\delta_{twist}CH_2$		
769.04	**40%**	$\delta_{rock'}CD_3$	**19%**	νC-O	**14%**	νCC	**14%**	$\delta_{rock}CD_3$		
838.77	**61%**	δ_{ip}COD	**20%**	νCC	**6%**	δ_sCD_3	**6%**	$\delta_{rock'}CD_3$		
1011.50	**46%**	δ_sCD_3	**20%**	νC-O	**19%**	δ_{ip}COD	**8%**	νCC		
1072.29	**72%**	$\delta_{as}CD_3$	**24%**	$\delta_{as'}CD_3$						
1073.79	**37%**	$\delta_{as'}CD_3$	**31%**	νC-O	**12%**	$\delta_{as}CD_3$	**7%**	δ_{ip}COD	**7%**	$\delta_{sciss}CH_2CO$
1098.25	**38%**	νC-O	**28%**	$\delta_{as'}CD_3$	**10%**	$\delta_{rock'}CD_3$	**9%**	$\delta_{as}CD_3$	**7%**	δ_{ip}COD
1125.47	**79%**	$\delta_{rock}CH_2$	**15%**	$\delta_{rock}CD_3$						
1180.18	**46%**	νCC	**44%**	δ_sCD_3						
1284.69	**96%**	$\delta_{twist}CH_2$								
1434.91	**85%**	$\delta_{wagg}CH_2$	**9%**	νCC						
1538.67	**95%**	$\delta_{sciss}CH_2$								
2197.72	**99%**	ν_sCD_3								
2320.26	**98%**	$\nu_{as}CD_3$								
2322.02	**98%**	$\nu_{as'}CD_3$								
2782.52	**100%**	νOD								
3016.84	**100%**	ν_sCH_2								
3049.94	**100%**	$\nu_{as}CH_2$								

gauche

ν [cm^{-1}]	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.	%	Int. coord.
195.28	**68%**	τCC	**29%**	δ_{oop}COD						
221.20	**62%**	δ_{oop}COD	**29%**	τCC						
375.85	**68%**	$\delta_{sciss}CH_2CO$	**20%**	$\delta_{rock'}CD_3$						
676.57	**47%**	$\delta_{rock}CD_3$	**25%**	drockCH2	**14%**	$\delta_{rock'}CD_3$	**9%**	$\delta_{twist}CH_2$		
755.00	**40%**	$\delta_{rock'}CD_3$	**17%**	$\delta_{rock}CD_3$	**16%**	νCC	**14%**	νC-O		
861.02	**63%**	δ_{ip}COD	**12%**	νCC	**8%**	$\delta_{rock}CH_2$	**6%**	δ_sCD_3		
978.67	**32%**	δ_sCD_3	**18%**	νCC	**14%**	δ_{ip}COD	**11%**	$\delta_{rock'}CD_3$	**10%**	$\delta_{sciss}CH_2CO$
	7%	νC-O	**6%**	$\delta_{rock}CH_2$						
1062.80	**60%**	νC-O	**16%**	$\delta_{as'}CD_3$	**9%**	$\delta_{as}CD_3$	**8%**	$\delta_{sciss}CH_2CO$		
1074.49	**65%**	$\delta_{as}CD_3$	**31%**	$\delta_{as'}CD_3$						
1088.27	**48%**	$\delta_{as'}CD_3$	**22%**	$\delta_{as}CD_3$	**19%**	νC-O	**7%**	$\delta_{rock'}CD_3$		
1157.17	**38%**	$\delta_{rock}CH_2$	**21%**	δ_sCD_3	**15%**	νCC	**10%**	$\delta_{rock}CD_3$	**8%**	δ_{ip}COD
1166.86	**35%**	δ_sCD_3	**34%**	νCC	**12%**	$\delta_{rock}CH_2$	**6%**	δ_{ip}COD		
1323.98	**90%**	$\delta_{twist}CH_2$								
1414.22	**89%**	$\delta_{wagg}CH_2$	**6%**	νCC						
1526.01	**95%**	$\delta_{sciss}CH_2$								
2189.66	**98%**	$\nu_{as}CD_3$								
2305.98	**96%**	$\nu_{as'}CD_3$								
2318.96	**98%**	$\nu_{as}CD_3$								
2772.36	**100%**	νOD								
3028.05	**100%**	ν_sCH_2								
3110.10	**99%**	$\nu_{as}CH_2$								