Electric Supplementary Information (ESI)

Intermolecular hydrogen bond stretching vibrations observed in terahertz spectra of crystalline vitamins

Masae Takahashi,[*,†,‡] *Nubuyuki Okamura,*[†,‡] *Xiaomeng Ding,*[†] *Hitoshi Shirakawa,*[†] *and Hiroaki Minamide*[‡]

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Table S1 Terahertz Vibrations of Vitamins **1**−**5**

compd	expt						calcd[a]		
	14 K		77K		RT		PBE-D		description
	freq[b]	fwhm[c]	freq[b]	fwhm[c]	freq[b]	ε[d]	freq[b]	int[e]	
1[f]							16.7	1.4	T_a
	34.8	3.0	35.2	3.7	34.3	13	39.2	15.4	R_c
	62.6	1.0	61.9	1.3	56.6	2	72.0	1.6	R_b
	69.5	1.1	68.9	1.5	64.3	4	76.1	5.4	$R_a+\nu$(N2H…N1)
	87.1	1.0	86.2	1.9	81.4	5	100.3	3.2	$T_b+\nu$(N2H…N1)
	97.5		96.8				100.6	1.4	$R_c+\nu$(C1H…O1)
	106.1	4.3	105.0	6.3	96.0	12	112.3	27.7	$R_b+\nu$(C1H…O1)
	115.9	1.9	115.2	2.3	107.1	9	121.1	2.1	τ(-$CONH_2$)
	128.2	9.9	127.4	10.1	120.9	18	137.1	34.6	τ(-$CONH_2$)
2							76.8	1.2	τ(-COOH)
							77.5	8.1	τ(-COOH)
	79.6	4.1	80.2	4.4			78.1	17.8	τ(-COOH)
	85.2	1.6	85.2	2.6	80.6	17	89.3	7.6	$R_c+\nu$(C1H…O1)
	94.2	6.3	93.5	6.6			102.9	21.2	R_b
	123.9	8.3	122.4	8.7	114.0	32	132.6	91.5	$T_a+\nu$(C5H…O1) + ν(O2H…N1)
							136.8	1.0	R_b
							136.8	4.8	$T_b+\nu$(C1H…O1) + ν(O2H…N1)
							139.4	5.0	T_c
	153.4	5.2			144.9	21	155.1	33.6	$R_c+\nu$(C5H…O1)
							158.0	23.9	R_a
3			64.6	1.6	60.0	9	63.5	2.8	T_a
			72.0	1.0	67.7	5	79.5	5.9	$T_c+\nu$(C6H…O2)
			76.2	0.8			92.9	1.2	$T_c+\nu$(C6H…O2)
			81.9	1.6	78.0	7	91.2	2.4	T_c
			85.8	1.1			98.2	2.6	T_b
			95.6	1.3	91.7	8	108.7	5.7	$R_a+\nu$(C6H…O2)
			100.6	1.0	96.0	8	107.5	2.3	R_c
			103.3	1.0			122.9	1.8	R_a
			105.3	1.1	102.0	7	115.4	2.3	$R_a+\nu$(C6H…O2)
			111.7	1.3	107.1	9	116.9	6.5	R_c

	124.3	2.3	120.0	20	132.7	18.1	γ
					135.1	3.7	γ
					143.2	10.2	R_b + ν(O6H…O3)
			138.0	16	153.2	50.6	R_b + ν(O3H…O5)
					157.2	4.9	R_b
			148.3	14	159.9	15.8	τ(-CH_2OH)
4	59.7	2.1	56.6	10	63.5	4.9	R_c+ν(C5H…O8)
	84.6	4.9	79.7	20	83.7	4.3	motion of Cl
	98.9	6.5	93.4	30	105.4	22.5	R_a
					106.1	2.3	T_c
					109.4	22.9	R_b
	123.7	7.1	114.9	51	124.0	73.2	motion of Cl + ν(O8H…Cl)
5					25.3	1.6	
	34.7	1.1	33.4	3	42.7	4.2	T_b
	44.8	1.8	43.7	11	51.4	5.8	T_c
	50.6						
	54.4	1.7	51.4	4	62.2	2.2	T_a
	60.4	1.7			73.3	4.3	τ(-COOH)
	64.3	2.4	58.3	5	75.3	2.9	τ(-COOH)
	69.6	3.8			79.5	1.4	τ(-COOH)
					82.1	3.7	R_b
	74.3	2.7	67.7	7	82.5	5.6	R_c + ν(N1H…O2)
					86.3	3.5	R_c
					90.0	4.2	R_a
	79.9	5.0	75.4	6	93.8	8.9	R_a + ν(C3H…N1)
					94.0	1.5	T_b
	97.0	5.4	92.6	9	104.0	13.2	Intramolecular motion
	104.4	2.6			104.4	8.5	Intramolecular motion
					116.5	4.4	T_b+ν(C4H…O3) + ν(N2H…O2)
	121.5	2.1	120.9	9	124.2	10.4	Intramolecular motion

[a]Calculated frequencies with an intensity greater than 1 km mol^{-1}. T_j: Intermolecular translation about the *j* axis; R_j: Intermolecular or lattice rotation about the *j* axis; ν: stretching; γ: out-of-plane bending; τ: torsion. [b]Frequency in cm^{-1}. [c]Full width at half maximum in cm^{-1}. [d]Molar extinction coefficient in M^{-1} cm^{-1}. [e]Intensity in km mol^{-1}. [f]Experimental result at 14 K and calculated data are from ref 24.

Table S2 Anharmonicity in the THz Vibrations of Vitamins **1**−**5**[a]

	displacement/Å		
compd	0.005	0.010	0.015
1[24]	39.2	39.6 (0.4)	41.0 (1.8)
	72.0	71.3 (–0.7)	71.1 (–0.9)
	76.1	74.9(–1.2)	73.3 (–2.8)
	100.3	99.7 (–0.6)	98.6 (–1.7)
	100.6	100.6 (0.0)	101.1 (0.5)
	112.3	112.0 (–0.3)	111.9 (–0.4)
	121.1	121.1 (0.0)	121.1 (0.0)
	137.1	137.2 (0.1)	137.5 (0.4)
2	76.8	75.6 (–1.2)	75.2(–1.6)
	77.5	77.4 (–0.1)	77.1 (–0.4)
	78.1	77.2 (–0.9)	76.6 (–1.5)
	89.3	89.2 (–0.1)	89.1(–0.2)
	102.9	102.3 (–0.6)	101.7(–1.2)
	132.6	133.1 (0.5)	133.8(1.2)
	136.8	136.3 (–0.5)	135.7(–1.1)
	136.8	136.6 (–0.2)	136.1(–0.7)
	139.4	139.0 (–0.4)	138.6(–0.8)
	155.1	154.9 (–0.2)	154.7(–0.4)
	158.0	157.7 (–0.3)	157.6(–0.4)
3	63.5	63.7 (0.2)	64.2 (0.7)
	79.5	79.2 (–0.3)	78.7 (–0.8)
	92.9	92.9 (0.0)	93.0 (0.1)
	91.2	91.0 (–0.2)	90.8 (–0.4)
	98.2	97.6 (–0.6)	96.7 (–1.5)
	107.5	107.6 (0.1)	107.4 (–0.1)
	108.7	108.7 (0.0)	108.6 (–0.1)
	115.4	115.7 (0.3)	116.0 (0.6)
	122.9	122.4 (–0.5)	121.9 (–1.0)
	116.9	117.0 (0.1)	117.2 (0.3)
	132.7	132.6 (–0.1)	132.2 (–0.5)
	135.1	135.1 (0.0)	134.8 (–0.3)
	143.2	143.1 (–0.1)	142.7 (–0.5)

	153.2	153.1 (–0.1)	152.8 (–0.4)
	157.2	157.2 (0.0)	157.0 (–0.2)
	159.9	160.2 (0.3)	160.2 (0.3)
4	63.5	63.7(0.2)	62.7 (–0.8)
	83.7	83.9 (0.2)	83.6 (–0.1)
	105.4	105.2 (–0.2)	104.3 (–1.1)
	106.1	106.1 (0.0)	105.3 (–0.8)
	109.4	109.0 (–0.4)	108.1 (–1.3)
	124.0	124.0 (0.0)	123.7 (–0.3)
5	42.7	42.8 (0.1)	41.6 (–1.1)
	51.4	49.6 (–1.8)	47.8 (–3.6)
	62.2	60.7 (–1.5)	59.9 (–2.3)
	73.3	73.2 (–0.1)	73.4 (0.1)
	75.3	75.0 (–0.3)	74.1 (–1.2)
	79.5	79.0 (–0.5)	78.1 (–1.4)
	82.1	82.1 (0.0)	81.8 (–0.3)
	82.5	81.4 (–1.1)	80.4 (–2.1)
	86.3	86.2 (–0.1)	85.9 (–0.4)
	90.0	89.7 (–0.3)	89.6 (–0.4)
	93.8	94.3 (0.5)	93.8 (0.0)
	94.0	93.6 (–0.4)	93.5 (–0.5)
	104.0	103.5 (–0.5)	103.1 (–0.9)
	104.4	103.9 (–0.5)	102.9 (–1.5)
	116.5	115.8 (–0.7)	115.0 (–1.5)
	124.2	123.5 (–0.7)	122.7 (–1.5)

[a]Frequencies in cm^{-1} at the respective amplitude of displacement from 0.005 to 0.015 Å. The difference from the frequency at 0.005 Å of the displacement amplitude is given in parentheses.