



Vibrational spectra and normal coordinate analysis of lithium pyruvate monohydrate and its isotopic compounds

Kazuhiko Hanai ^{a,*}, Akio Kuwae ^a, Ko-Ki Kunimoto ^b and Soh-ichi Kitoh ^b

^a Graduate School of Natural Sciences, Nagoya City University, Mizuho-Ku, Nagoya 467-8501, Japan

^b Division of Material Sciences, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-Machi, Kanazawa 920-1129, Japan

*Corresponding author at: Graduate School of Natural Sciences, Nagoya City University, Mizuho-Ku, Nagoya 467-8501, Japan.
Tel.: +81.52.8725856. Fax: +81.52.8725857. E-mail address: hanai@nsc.nagoya-cu.ac.jp (K. Hanai).

ARTICLE INFORMATION



DOI: 10.5155/eurjchem.5.2.305-310.1004

Received: 18 December 2013

Received in revised form: 31 January 2014

Accepted: 01 February 2014

Online: 30 June 2014

KEYWORDS

Gem-Diol form
Isotope shifts
IR spectroscopy
Raman spectroscopy
Normal coordinate analysis
Lithium pyruvate monohydrate

ABSTRACT

IR and Raman spectra of lithium pyruvate monohydrate and its O- and C-deuterated and ¹³C- and ¹⁸O-substituted compounds have been recorded in the solid state, and the observed bands have been assigned by using the isotope effects and the normal coordinate calculations based on the *gem*-diol structure (lithium 2,2-dihydroxypropionate). The refined force constants have well reproduced the observed frequencies and the ¹³C- and ¹⁸O-shifts. These results support the structures of these compounds discussed by many authors. The potential energy distributions show that many vibrational modes are very complicated except for the well-known group vibrations. The additive property of the isotopic frequency shifts has also been discussed.

Supplementary material

Table S1. Calculated frequencies and isotope shifts (cm⁻¹)^a for Li-Pyr· H₂O.

Calcd.	$\Delta\nu_a$	$\Delta\nu_b$	$\Delta\nu_c$	$\Delta\nu_d$	$\Delta\nu_e$	$\Delta\nu_f$	$\Delta\nu_g$	P. E. D. (%) ^b
<i>A'</i>								
3037.6	0.0	0.0	0.0	-10.0	0.0	-10.0	-10.0	OH str. (100)
3004.3	0.0	-0.1	-10.8	-0.1	0.0	0.0	-0.1	CH ₃ asym. str. (100)
2946.0	0.0	-0.3	-2.7	0.0	-0.3	0.0	-0.3	CH ₃ sym. str. (99)
1529.8	-7.1	-15.8	-0.2	-6.2	-15.9	-6.3	-22.1	OH bend (55), C _{(1)C(2)} str. (28), OCO wag (12),
1447.1	-1.1	-0.3	-1.0	-0.6	-0.4	-0.7	-1.0	CH ₃ asym. def. (78), CH ₃ rock (12)
1406.3	-33.0	-0.7	-0.1	-3.8	-0.8	-3.9	-4.6	CO ₂ sym. str. (33), OH bend (23), CO ₂ ⁻ bend (21), C _{(1)C(2)} str. (17)
1368.3	-1.9	-1.3	-5.8	-0.2	-1.2	-0.1	-1.4	CH ₃ sym. def. (101)
1147.6	-1.0	-16.7	-9.2	-2.2	-17.0	-2.5	-19.2	CH ₃ rock (36), C _{(2)C(3)} str. (33), OCO sym. str. (30), CCC bend (15)
1117.3	-1.5	-17.9	-13.1	-4.4	-17.1	-3.6	-21.5	C _{(2)C(3)} str. (78), OCO wag (31), C _{(1)C(2)} str. (12), OH bend (10)
944.0	-0.2	-7.7	-3.2	-15.0	-8.1	-15.4	-23.1	OCO sym. str. (65), CH ₃ rock (30)
891.2	-1.1	-0.7	-0.1	-8.2	-1.7	-9.2	-9.9	OH tor. (86), OCO sym. str. (10)
837.1	-8.6	-1.3	-0.4	-3.6	-0.8	-3.1	-4.4	CO ₂ ⁻ sym. str. (33), CO ₂ ⁻ o. p. bend (25), C _{(1)C(2)} str. (10)
792.6	-11.9	-2.1	-6.0	-2.9	-1.9	-2.7	-4.8	CO ₂ ⁻ o. p. bend (28), OCO wag (23), C _{(1)C(2)} str. (18), C _{(2)C(3)} str. (14)
670.3	-3.3	-3.4	-0.7	-7.0	-3.6	-7.2	-10.6	CO ₂ ⁻ bend (37), OCO wag (28), OCO sym. str. (11), CO ₂ ⁻ sym. str. (10)
466.1	-1.4	-1.8	-1.0	-8.9	-1.5	-8.6	-10.4	OCO wag (42), CO ₂ ⁻ bend (21), OCO bend (20), CO ₂ ⁻ o.p. bend (14), C _{(1)C(2)} str. (12)
417.6	-0.1	-0.9	-0.9	-16.9	-1.0	-17.0	-17.9	OCO bend (91), OCO wag (18), C _{(1)C(2)} str. (16), OCO sym. str. (13)
266.2	-0.2	-0.7	-4.2	-1.5	-0.6	-1.4	-2.1	CCC bend (82), C _{(1)C(2)} str. (23), CO ₂ ⁻ o.p. bend (14)
<i>A''</i>								
3037.0	0.0	0.0	0.0	-9.8	-0.1	-9.9	-9.9	OH str. (100)
3005.3	0.0	0.0	-10.9	0.0	0.0	0.0	0.0	CH ₃ asym. str. (100)
1603.7	-46.5	-0.3	0.0	-0.4	-0.3	-0.4	-0.7	CO ₂ ⁻ antisym. (87), CO ₂ ⁻ rock (12)
1454.8	-0.4	-1.0	-0.9	-0.5	-0.9	-0.4	-1.4	CH ₃ asym. def. (79), CH ₃ rock (15)
1376.5	0.0	-0.6	0.0	-9.6	-0.5	-9.5	-10.1	OH bend (99)
1186.5	-0.1	-24.1	-4.8	-6.3	-23.7	-5.9	-30.0	OCO antisym. str. (67), OCO rock (40), CH ₃ rock (32), CH ₃ asym. def. (10)
967.7	0.0	-5.4	-5.5	-12.8	-6.9	-14.3	-19.7	OCO antisym. str. (56), CH ₃ rock (50)
899.8	0.0	0.0	0.0	-4.8	0.0	-4.8	-4.8	OH tor. (96)
592.2	-0.6	-4.0	-0.8	-15.0	-3.2	-14.2	-18.2	OCO rock (78), CO ₂ ⁻ rock (23)
537.4	-0.8	-0.1	-4.0	-11.6	0.0	-11.5	-11.6	OCO twist (74), CO ₂ ⁻ rock (11)
348.8	-0.4	-0.2	0.0	-7.2	-0.2	-7.2	-7.4	CO ₂ ⁻ rock (55), OCO twist (21), OCO rock (11)

^a See the footnote to Table 1 in the text.^b The values less than 10% were omitted.**Table S2.** Calculated frequencies (cm⁻¹) and isotope shifts^a for Li-Pyr· D₂O.

Calcd.	$\Delta\nu_a'$	$\Delta\nu_b'$	$\Delta\nu_c'$	P. E. D. (%) ^b
<i>A'</i>				
3004.3	0.0	-0.1	-10.8	CH ₃ asym. str. (100)
2946.0	0.0	-0.3	-2.7	CH ₃ sym. str. (99)
2214.1	0.0	0.0	0.0	OD str. (100)
1468.7	-10.4	-7.6	0.0	C _{(1)C(2)} str. (36), CH ₃ asym. def. (25), CO ₂ ⁻ sym. str. (17), CO ₂ ⁻ bend (12), CH ₃ rock (11)
1443.4	-21.7	-1.7	-1.0	CH ₃ asym. def. (54), C _{(1)C(2)} str. (14), CO ₂ ⁻ sym. str. (13)
1371.4	-5.0	-1.2	-5.1	CH ₃ sym. def. (95)
1273.9	-5.8	-21.3	-3.7	OD bend (29), OCO wag (26), CO ₂ ⁻ sym. str. (10)
1141.4	-2.2	-20.8	-13.9	C _{(2)C(3)} str. (82), OCO sym. str. (20), CH ₃ rock (18), CCC bend (13), OCO wag (10)
1022.1	-0.3	-1.7	-7.1	OD bend (43), C _{(2)C(3)} str. (23), CH ₃ rock (20), OCO sym. str. (12)
937.8	-0.1	-8.6	-3.1	OCO sym. str. (72), CH ₃ rock (32)
837.2	-12.8	-0.6	-1.0	CO ₂ ⁻ o.p. bend (34), CO ₂ ⁻ sym. str. (31)
769.2	-11.0	-1.0	-3.5	CO ₂ ⁻ o.p. bend (26), C _{(1)C(2)} str. (20), CO ₂ ⁻ sym. str. (19), CO ₂ ⁻ bend (14), OCO wag (11), C _{(2)C(3)} str. (10)
668.5	-0.5	-1.2	-0.5	OD tor. (79), OCO wag (22)
624.1	-0.8	-3.0	-0.9	CO ₂ ⁻ bend (26), OD tor. (24), OCO wag (19)
455.3	-1.4	-1.5	-1.1	OCO wag (41), CO ₂ ⁻ bend (20), CO ₂ ⁻ o. p. bend (14), OCO bend (13), C _{(1)C(2)} str. (12)
405.9	-0.1	-0.9	-0.9	OCO bend (92), OCO wag (17), C _{(1)C(2)} str. (13), OCO sym. str. (12)
265.8	-0.2	-0.7	-4.2	CCC bend (82), C _{(1)C(2)} str. (23), CO ₂ ⁻ o. p. bend (14)
<i>A''</i>				
3005.4	0.0	-0.1	-11.0	CH ₃ asym. str. (100)
2212.2	-0.1	0.0	0.0	OD str. (100)
1603.0	-46.5	-0.3	0.0	CO ₂ ⁻ antisym. str. (87), CO ₂ ⁻ rock (12)
1454.2	-0.3	-0.9	-0.9	CH ₃ asym. def. (80), CH ₃ rock (15)
1200.5	0.0	-24.1	-3.6	OCO antisym. str. (77), OCO rock (38), CH ₃ rock (25), CH ₃ asym. def. (10)
1040.9	0.0	-0.1	-4.0	OD bend (64), CH ₃ rock (28)
934.5	0.0	-6.3	-2.6	OCO antisym. str. (44), CH ₃ rock (31), OD bend (25)
686.0	0.0	-0.3	-0.6	OD tor. (77), OCO rock (14)
575.3	-0.9	-3.1	-0.1	OCO rock (56), CO ₂ ⁻ rock (30), OD tor. (10)
513.0	-0.5	-0.1	-4.1	OCO twist (62), OD tor. (12), OCO rock (10)
341.5	-0.4	-0.3	0.0	CO ₂ ⁻ rock (53), OCO twist (23), OCO rock (11)

^a See the footnote to Table 2 in the text.^b The values less than 10% were omitted.

Table S3. Calculated frequencies (cm⁻¹) for Li-Pyr-d₃·H₂O.

Calcd.	P. E. D. (%) ^a
A'	
3037.6	OH str. (100)
2225.8	CD ₃ asym. str. (101)
2114.2	CD ₃ sym. str. (98)
1520.9	OH bend (60), C _{(1)C(2)} str. (30), OCO wag (12)
1406.7	CO ₂ ⁻ sym. str. (34), OH bend (23), CO ₂ ⁻ bend (21), C _{(1)C(2)} str. (17)
1129.0	C _{(2)C(3)} str. (106), CD ₃ sym. def. (28), OCO wag (18)
1097.6	OCO sym. str. (64), CD ₃ rock (17), CCC bend (15), C _{(1)C(2)} str. (13), OCO bend (10)
1037.2	CD ₃ sym. def. (52), CD ₃ asym. def. (19), OCO wag (14)
1026.5	CD ₃ asym. def. (69), OCO wag (13)
892.8	OH tor. (99)
861.2	CO ₂ ⁻ sym. str. (31), OCO sym. str. (27), CO ₂ ⁻ o. p. bend (11)
789.5	CO ₂ ⁻ o. p. bend (32), CD ₃ rock (20), OCO sym. str. (13), OCO wag (11)
747.6	CD ₃ rock (22), CO ₂ ⁻ bend (21), CO ₂ ⁻ sym. str. (20), C _{(1)C(2)} str. (16), C _{(2)C(3)} str. (12), CO ₂ ⁻ o.p. bend (13)
632.3	OCO wag (24), CD ₃ rock (23), CO ₂ ⁻ bend (23)
461.7	OCO wag (40), CO ₂ ⁻ bend (21), CO ₂ ⁻ o.p. bend (15), C _{(1)C(2)} str. (13), OCO bend (12)
412.9	OCO bend (95), OCO wag (26), C _{(1)C(2)} str. (16), OCO sym. str. (11)
244.3	CCC bend (82), C _{(1)C(2)} str. (21), CO ₂ ⁻ o.p. bend (13)
A''	
3037.0	OH str. (100)
2228.3	CD ₃ asym. str. (101)
1602.8	CO ₂ ⁻ antisym. str. (87), CO ₂ ⁻ rock (12)
1377.7	OH bend (100)
1154.3	OCO antisym. str. (97), OCO rock (44), CD ₃ rock (16)
1037.0	CD ₃ asym. def. (89)
902.7	OH tor. (90)
808.1	CD ₃ rock (63), OCO antisym. str. (19)
565.6	OCO rock (44), CO ₂ ⁻ rock (35), OCO twist (17), CD ₃ rock (11), CO ₂ ⁻ antisym. str. (10)
498.9	OCO twist (55), OCO rock (25)
347.9	CO ₂ ⁻ rock (54), OCO twist (20), OCO rock (13)

^a The values less than 10% were omitted.**Table S4.** Calculated frequencies (cm⁻¹) for Li-Pyr-d₃·D₂O.

Calcd.	P. E. D. (%) ^a
A'	
2225.9	CD ₃ asym. str. (100)
2214.0	OD str. (99)
2114.1	CD ₃ sym. str. (98)
1454.6	C _{(1)C(2)} str. (52), CO ₂ ⁻ sym. str. (32), CO ₂ ⁻ bend (22)
1268.2	OD bend (36), OCO wag (32), CO ₂ ⁻ sym. str. (11), C _{(2)C(3)} str. (11)
1120.5	C _{(2)C(3)} str. (99), CD ₃ sym. def. (24), OCO sym. str. (14), CCC bend (11)
1081.6	CD ₃ sym. def. (42), OCO sym. str. (42)
1031.1	CD ₃ asym. def. (84)
953.8	OD bend (35), CD ₃ sym. def. (27), OCO sym. str. (25), C _{(1)C(2)} str. (10)
846.8	CO ₂ ⁻ sym. str. (33), CO ₂ ⁻ o.p. bend (17), OCO sym. str. (12)
785.5	CD ₃ rock (39), CO ₂ ⁻ o. p. bend (26), OCO sym. str. (13)
746.5	CO ₂ ⁻ bend (22), CO ₂ ⁻ sym. str. (21), CO ₂ ⁻ o.p. bend (17), C _{(1)C(2)} str. (16), CD ₃ rock (15), C _{(2)C(3)} str. (12)
663.7	OD tor. (91), OCO wag (15)
595.0	CO ₂ ⁻ bend (23), OCO wag (18), CD ₃ rock (15), C _{(1)C(2)} str. (14), OD tor. (10)
450.1	OCO wag (40), CO ₂ ⁻ bend (20), CO ₂ ⁻ o.p. bend (15), C _{(1)C(2)} str. (12)
401.2	OCO bend (95), OCO wag (25), C _{(1)C(2)} str. (13), OCO sym. str. (11)
244.0	CCC bend (82), C _{(1)C(2)} str. (21), CO ₂ ⁻ o.p. bend. (13)
A''	
2228.4	CD ₃ asym. str. (100)
2212.0	OD str. (99)
1602.2	CO ₂ ⁻ antisym. str. (87), CO ₂ ⁻ rock (12)
1179.0	OCO antisym. str. (99), OCO rock (37), OD bend (16), CD ₃ rock (12)
1036.2	CD ₃ asym. def. (90)
1007.0	OD bend (79), OCO rock (10)
807.3	CD ₃ rock (56), OCO antisym. str. (25)
667.4	OD tor. (86)
560.2	OCO rock (41), CO ₂ ⁻ rock (37), OCO twist (18), CO ₂ ⁻ antisym. str. (11)
476.4	OCO twist (49), OCO rock (25)
340.8	CO ₂ ⁻ rock (52), OCO twist (22), OCO rock (13)

^a The values less than 10% were omitted.

Table S5. Force constants ^a for the pyruvate ion in the diol form.

$K(\text{OH})$	4.970	$H(\text{C}_{(2)}\text{C}_{(1)}\text{O})$	0.534	$f[\gamma(\text{CO}_2^-)]$	0.538
$K(\text{CH})$	4.433	$H(\text{OC}_{(1)}\text{O})$	0.772	$f[\tau(\text{OH})(a')]$	0.123
$K(\text{C}=\text{O})$	6.754	$F(\text{HCH})$	0.072	$f[\tau(\text{OH})(a'')]$	0.125
$K(\text{CO})$	2.864	$F(\text{CCH})$	0.757	$f_1[\Delta r(\text{C}_{(1)}\text{O}), \Delta r(\text{C}_{(1)}\text{O}')]]$	0.002
$K(\text{C}_{(1)}\text{C}_{(2)})$	2.020	$F(\text{C}_{(1)}\text{C}_{(2)}\text{O})$	2.349	$f_2[\Delta\delta(\text{C}_{(1)}\text{C}_{(2)}\text{O}), \Delta\delta(\text{C}_{(3)}\text{C}_{(2)}\text{O})]$	0.015
$K(\text{C}_{(2)}\text{C}_{(3)})$	2.172	$F(\text{C}_{(3)}\text{C}_{(2)}\text{O})$	1.536	$f_3[\Delta\delta(\text{C}_{(1)}\text{C}_{(2)}\text{O}), \Delta\delta(\text{OC}_{(2)}\text{O})]$	-0.366
$H(\text{HCH})$	0.408	$F(\text{C}_{(2)}\text{OH})$	0.401	$f_4[\Delta\delta(\text{C}_{(3)}\text{C}_{(2)}\text{O}), \Delta\delta(\text{OC}_{(2)}\text{O})]$	0.289
$H(\text{CCH})$	0.168	$F(\text{OC}_{(2)}\text{O})$	0.492	$f_5[b(\text{OC}_{(2)}\text{O}), \tau(\text{OH})(a')]$	-0.088
$H(\text{C}_{(1)}\text{C}_{(2)}\text{O})$	0.138	$F(\text{C}_{(1)}\text{C}_{(2)}\text{C}_{(3)})$	0.013	$f_6[w(\text{OC}_{(2)}\text{O}), b(\text{CO}_2^-)]$	0.119
$H(\text{C}_{(3)}\text{C}_{(2)}\text{O})$	0.379	$F(\text{C}_{(2)}\text{C}_{(1)}\text{O})$	0.337	$f_7[r(\text{CH}_3), t(\text{OC}_{(2)}\text{O})]$	0.163
$H(\text{C}_{(2)}\text{OH})$	0.537	$F(\text{OC}_{(1)}\text{O})$	0.266	$f_8[r(\text{OC}_{(2)}\text{O}), r(\text{CO}_2^-)]$	-0.458
$H(\text{OC}_{(2)}\text{O})$	0.402	$\kappa(\text{C}_{(2)})$	0.070		
$H(\text{C}_{(1)}\text{C}_{(2)}\text{C}_{(3)})$	0.358	$\kappa(\text{C}_{(3)})$	-0.042		

^a These constants were obtained by using the IR frequencies mostly as observed data in the least squares method. When the IR bands were not observed, the corresponding Raman data were used. K , H , F , and f_1 in $\text{mdyn}/\text{\AA}$ (10^2 N/m). κ , f 's and f_2 to f_8 in $\text{mdyn}\cdot\text{\AA}$ (10^{-18} Nm). In the three f constants, γ and τ designate out-of-plane bending and torsion, respectively. The constants, f_1 to f_8 , are interaction terms, and w , b , r , and t denote wagging, bending, rocking, and twisting, respectively.