STUDIES ON THE RAMAN EFFECT OF ORGANIC SUBSTANCES. VII. RAMAN EFFECT OF FURANE DERIVATIVES.

By Kwan HAN.

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Introduction. In one of the previous papers[1], the Raman spectra of α-mono-derivatives of furane were reported. Nearly at the same time, some of the furane derivatives were also studied by Bonino and Ansidei[2] and by Médard[3]. In the present investigation the Raman spectra of some α-mono-derivatives, α, α'-di-derivatives and α, β-di-derivatives, which have not been reported hitherto, have been studied in order to confirm the characteristic frequencies attributable to the furane ring and to study the constitutive influences exerted upon them. The more complete investigation will be reported after studying the other poly-substitution products of furane, which are now in the course of experiments.

Experimental. The substances used were synthesized by the following processes. α-Furfuryl methyl ether (I) (b. p. 134–136°) and α-furfuryl ethyl ether (II) (b. p. 148–150°) were prepared by Wissell-Tollens' method[4], that is, by warming the mixtures of α-furfuryl alcohol, F–CH_2OH,[5] and the corresponding alkyl iodides with potassium hydroxide. The ethers obtained were dried over calcium chloride and then fractionated over metallic sodium.

α-Furfuryl-acetone (III) (b. p. 101–102°/21 mm.) was obtained by reducing furfurylidene-acetone, F–CH : CH·CO·CH_3,[5] with 2.5% sodium amalgam in acetic acid solution, according to Harries and Kaiser[6].

α-Furyl-ethylene (IV) (b. p. 99°) was obtained by the decarboxylation of α-furfuracrylic acid, F–CH : CH·COOH[5], at about 260°C. The substance obtained was washed with aqueons sodium carbonate and dried over anhydrous sodium sulphate[7].

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(1) This Bulletin, **9** (1934), 327.

(2) G. B. Bonino and R. Manzoni-Ansidei, *Z. physik. Chem.*, B, **25** (1934), 327.

(3) L. Médard, *Bull. soc. chim.*, (5), **1** (1934), 934.

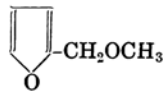
(4) L. von Wissell and V. Tollens, *Ann.*, **272** (1893), 297.

(5) F denotes α-furyl-group  – in this paper.

(6) C. Harries and Friedrich Kaiser, *Ber.*, **32** (1893), 1320.

(7) C. Liebermann, *Ber.*, **27** (1894), 287.

α-Furyl cyanide (V) (b. p. 146–147°) was prepared by treating α-furfuraldoxime, F–CH : NOH, with acetic anhydride according to Pinner[8].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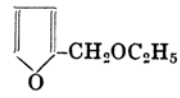
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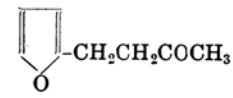
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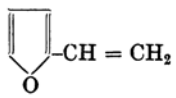
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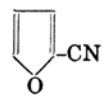
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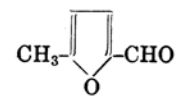
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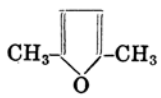
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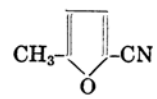
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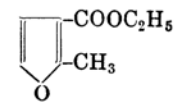
IX

2-Methyl-furfural-(5)[9] (VI) (b. p. 83–85°/15 mm.) was prepared by reducing a mixture of hydrochloric acid (sp. gr. 1.173) and ordinary sugar with stannous chloride.

2,5-Dimethyl-furane (VII) (b. p. 93°) was prepared by dropping small pieces of potassium hydroxide into a mixture of 2-methyl furfural-(5), hydrazine hydrate and methyl alcohol under sufficient cooling (Wolff-Kischner's method)[10]. The substance obtained was washed with a saturated aqueous solution of calcium chloride and sodium bisulphite. It was, then, dehydrated over calcium chloride and redistilled over metallic sodium under normal pressure.

2-Methyl-furyl cyanide-(5)[11] (VIII) (b. p. 65°/10 mm.) was prepared from α-furfuryl chloride and aqueous potassium cyanide. α-Furfuryl chloride[12] was obtained by treating α-furfuryl alcohol with thionyl chloride and pyridine in absolute ether.

Ethyl 2-methyl-furoate-(3)[13] (IX) (b. p. 100–101°/25 mm.) was prepared by treating a mixture of 1,2-dichlorether (b. p. 140–145°) and ethyl acetoacetate with aqueous sodium hydroxide.

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(8) A. Pinner, *Ber.*, **25** (1892), 1415.
(9) "Organic Syntheses", Vol. XIV, p. 62 (1934).
(10) This Bulletin, **9** (1934), 327.
(11) T. Reichstein, *Ber.*, **63** (1930), 749.
(12) W. R. Kirner, *J. Am. Chem. Soc.*, **50** (1928), 1955.
(13) H. Gilman and R. Robert, *Rec. trav. chim.*, **51** (1932), 408.

About 3–10 c.c. of each sample was used. The Raman spectra were taken by means of a spectrograph with three prisms[1]. The results are shown in Table 1. The numbers of the Raman lines(n), the number of the plates, and the conditions under which the spectra were taken, are summarized in Table 2. 2,5-Dimethyl-furane has been studied by Bonino and Manzoni-Ansidei[2]. Their results are in good agreement with those reported in the present paper. On account of the colouration, the Raman spectrum of 2-methyl-furfural-(5) (VI) could not be observed completely, except some of the intense lines, viz., $\Delta\nu$ 1355, 1375, 1521, 1590, 1675 and 3122 cm^{-1}. The all data and the photograph of this substance are omitted in this paper.

Table 1. The $\Delta\nu$ Values of the Raman Spectra of Furane Derivatives.

(1) α-Furfuryl methyl ether (I).

140 (3b, d); 166 (3); 383 (3bb, d); (433) (0)?; 466 (2); (604) (1/2); 627 (4d); 642 (3); (740) (1bb, d); (819) (1bb, d); 883 (5); 901 (4); 920 (4); 951 (5b, d); 1018 (4); 1077 (8); 1150 (5); 1224 (6d); (1291) (1); 1384 (8b); 1445 (3d); (1473) (1/2)?; 1501 (10); 1593 (6d); 2819 (5); 2841 (0); 2894 (1/2); 2938 (1); 2985 (1/2); 3116 (6b, d); 3141 (2).

(2) α-Furfuryl ethyl ether (II).

(167) (1b, d); 351 (2); (384) (0); 627 (2); (640) (0); (807) (0d)?; 840 (2); 887 (3); 923 (3); (971) (1d); 1018 (3d); 1078 (6d); 1150 (2); 1223 (5b, d); 1384 (6d); 1444 (3b, d); 1501 (10); 1594 (5d); 2930 (5); 2974 (4); 3115 (6b, d); 3145 (5).

(3) α-Furfuryl-acetone (III).

625 (0); 650 (1/2d); 732 (1/2)?; 748 (1); 807 (0)?; 876 (1d); 938 (1d); 1020 (1/2); 1041 (2b, d); 1083 (5); 1150 (5bb, d); (1209) (1d); 1250 (1/2); 1292 (1/2)?; 1388 (4d); 1412 (1/2); 1446 (1d); 1477 (2); 1509 (10); 1597 (6d); 1679 (2); 1721 (3); 2918 (3); 2974 (1/2); 3120 (4d); (3155) (4d).

(4) α-Furyl-ethylene (IV).

217 (6); (368) (1/2b, d); 481 (5); 655 (5); 716 (2d); (736) (1/2b, d); (811) (1d); 885 (3); 908 (1); 925 (4); 1002 (1); (1017) (1/2); 1027 (8); 1079 (4d); 1145 (3b, d); 1216 (5); 1255 (3); 1292 (8d); 1387 (8); 1491 (10); 1576 (4); 1642 (10); 3004 (1/2); 3125 (3); (3154).

(5) α-Furyl cyanide (V).

183 (8); (311) (1/2); 570 (8s); 591 (1s); 640 (5); 655 (4); 761 (1d); 837 (2d); 887 (6d); 928 (6); 938 4b); 1020 (7); 1072 (8); 1151 (8); 1232 (6); 1379 (10); (1456) (2); 1471 (10b); 1566 (6); 2233 (10); 3133 (5d); 3156 (3).

(6) 2,5-Dimethyl-furane (VII).

266 (2d); 290 (1d); 396 (0); (445) (1/2); 610 (5); 689 (1); 781 (0); 923 (1/2); 991 (2); 1018 (3); 1086 (2b, d); 1217 (5d); (1269) (1); 1351 (2); 1379 (2); 1452 (4d); 1503 (1); 1573 (8); 2926 (6d); 2956 (1/2d); 2975 (1/2); 3118 (3).

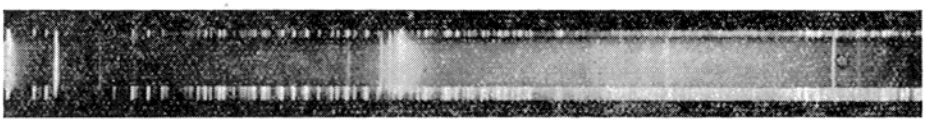
Table 1. (*Concluded*)

(7) 2-Methyl-furyl cyanide-(5) (VIII).

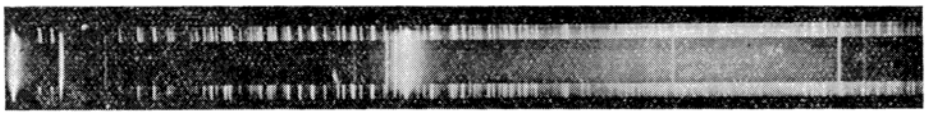
164 (4d); 260 (2d); 343 ($^1/_2$d); 386 (2d); 433 ($^1/_2$); 493 ($^1/_2$); 616 (1); 649 (3); 675 (0); 952 ($^1/_2$); 999 (1); 1028 (5); 1202 (4); 1223 (2); 1356 (3d); 1388 (2); 1449 ($^1/_2$); 1507 (2); 1523 (10); 1570 (0); 1600 (6); 2231 (8); 2932 (4); 2977 ($^1/_2$); 3120 (3d).

(8) Ethyl 2-methyl-furoate-(3) (IX).

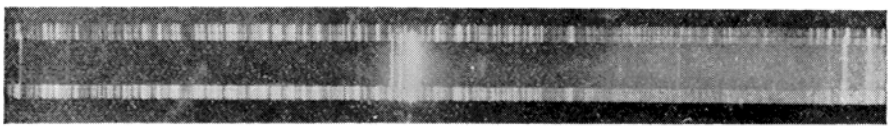
327 (1d); 359 (1d); 609 (2); 638 (3b); 684 (4b); 775 (2); 833 (1d); 869 (4d); 899 (6); 948 (2); 1013 (3d); 1041 (6); 1236 (2d); 1304 (6); 1345 (2); 1372 (2); 1396 (3); 1415 (3); 1453 (4b, d); 1522 (10); 1603 (6b, d); 1716 (6b, d); 2932 (8b, d); 2979 (3b, d); (3120) (4d); 3157 ($^1/_2$).



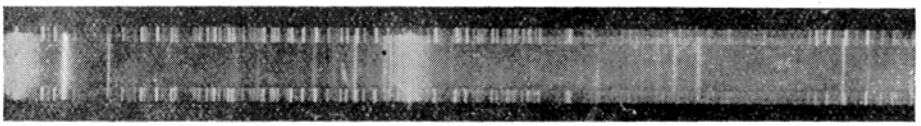
(1) α-Furfuryl methyl ether (I)



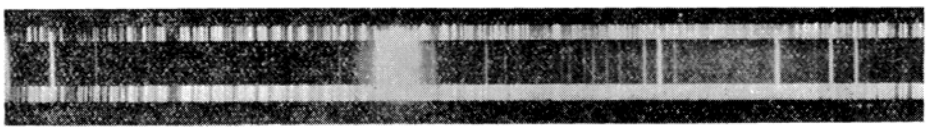
(2) α-Furfuryl ethyl ether (II)



(3) α-Furfuryl-acetone (III)

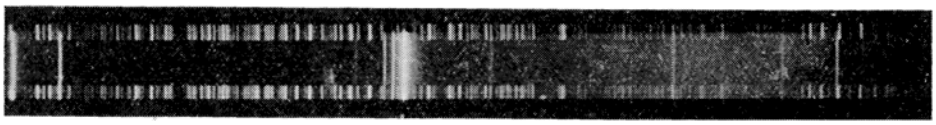


(4) α-Furyl-ethylene (IV)

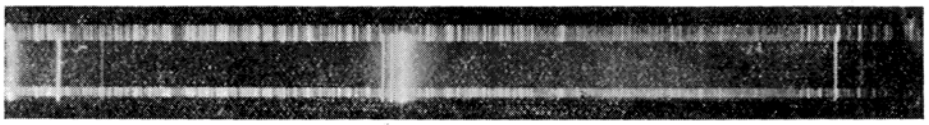


(5) α-Furyl cyanide (V)

(6) 2, 5-Dimethyl-furane (VII)



(7) 2-Methyl-furyl cyanide-(5) (VIII)



(8) Ethyl 2-methyl-furoate-(3) (IX)

Table 2.

Substance	n	No. of plates	Width of slit (10^{-2} mm.)	Temp. (°C.)	t (hours)
α-Furfuryl methyl ether (I)	56	210	70	23	8
		211	64	23	10
α-Furfuryl ethyl ether (II)	44	221	70	30	8
		222	64	30	10
α-Furfuryl-acetone (III)	29	257	75	25	8
α-Furyl ethylene (IV)	53	231	70	28	6
α-Furyl cyanide (V)	44	225	70	30	8
		226	64	30	10
		290	75	24	5
		291	70	25	14
2,5-Dimethyl-furane (VII)	36	328	70	26	6
		329	70	25	8
2-Methyl-furyl cyanide-(5) (VIII)	39	229	70	28	6
		230	70	28	8
Ethyl 2-methyl-furoate-(3) (IX)	38	247	70	26	6
		248	64	26	8
		256	64	25	8

Discussion. The Raman lines corresponding to ω_1 626, ω_2 885, ω_3 923, ω_4 1018, ω_5 1083, ω_6 1150, ω_7 1223, ω_8 1384, ω_9 1505, ω_{10} 1602, ω_{11} 3117, and ω_{12} 3150 cm.$^{-1}$ in α-furfuryl-acetone (III), α-furfuryl methyl ether (I), and α-furfuryl ethyl ether (II) are in good coincidence with those in α-methyl-furane, F–CH_3, α-furfuryl alcohol, F–CH_2·OH, and α-furfuryl acetate, F–CH_2·O·CO·CH_3, which have been reported in Part III[1] (See Table 3). As to the other α-furyl- and furoyl-compounds, such as α-furyl-ethylene, α-furyl cyanide and alkyl furoates, these characteristic frequencies are also nearly constant, excepting ω_9 and ω_{10} (Table 4). The frequency of ca. 960 cm.$^{-1}$ and those in the region of $\Delta\nu$ 810 and 740 cm.$^{-1}$ appear also in most of the α-mono-derivatives of furane.

It is remarkable that the intense lines at ω_2 885, ω_6 1150 and ω_{12} 3150 cm.$^{-1}$ in α-mono-derivatives, are not observed in the α, α'-di-derivatives of furane, such as 2,5-dimethyl-furane and 2-methyl-furyl cyanide-(5). The intense line corresponding to ω_5 1083 cm.$^{-1}$ in α-mono-derivatives disappears in 2-methy-furyl cyanide-(5) and appears weakly in 2,5-dimethyl-furane, while a new line corresponding to $\Delta\nu$ 1355 cm.$^{-1}$ is observed in the α, α'-di-derivatives.

It is of interest to note that, in the case of α-mono-derivatives of furane, two frequencies, ω_9 and ω_{10}, in the region between 1460 and 1600 cm.$^{-1}$ are slightly reduced by the constitutive influence of the unsaturated side chain attached to the furane ring. As shown below in Table 6, in passing from α-methyl-furane to α-furyl-ethylene and α-furyl cyanide, the corresponding frequenies, ω_9 and ω_{10}, are reduced about 20 in wave numbers.

The frequencies in question in other furane derivatives which have been observed hitherto, are summarized in Table 5. A glance at Table 5 will lead to the conclusion that, in α-furfuryl-compounds, F–CH_2–X, ω_9 and ω_{10} remain nearly constant, while in the furfurlidene-compounds, F–CH = CH–X, a slight decrease of ω_9 is found. The mean values of ω_9 and ω_{10} are taken as $\Delta\nu$ 1505 and 1600 cm.$^{-1}$ for furfuryl, and $\nu\Delta$ 1480 and 1575 cm.$^{-1}$ for furfurlidene- or furoyl-compounds, while the corresponding ones in furyl cyanide are $\Delta\nu$ 1471 and 1566 cm.$^{-1}$

Table 3. Raman Spectra of α-Furfuryl-compounds. (F : )

	F-CH_3	F-CH_2·CH_2·$COCH_3$	F-CH_2·OH	F-CH_2·O·CO·CH_3	F-CH_2·OCH_3	F-CH_2·OC_2H_5
	253 343		177 421	172 193 315 332	140 166 383 469	167 351 384
ω_1	626 654	625 650	603 626	621 659	604 627 642	627 640
	718	732 748	741	745		
	796 (855)	807	816	835	819	796
ω_2	888	876	888	886	883	885
ω_3	917 (976)	938	922 959	924 964	901 920 951	923
ω_4	1018	1018	1018	1022	1017	1018
ω_5	1084	1083	1083	1083	1077	1078
ω_6	1147	1150	1154	1153	1150	1150
ω_7	1215	1209	1228	1231	1224	1223
ω_8	(1376 1389	1390	(1374 1391	1389	1384	1394
Δ	1453	1446 1477	1477	1450	1473	1453
ω_9	1510	1509	1507	1505	1501	1501
ω_{10}	1605	1597	1602	1604	1593	1594
	2745 2888 2928 2955 3000	2811 2976	2940	2946	2821 2841 2939	2930 2974
ω_{11}	3119	3117	3117	3130	3116	3115
ω_{12}	3153	3160	3154	3156	3141	3145

Table 4. Raman Frequencies of α-Furoyl- and α-Furyl-compounds. (F: )

	F-CO·OCH$_3$	F-CO·Cl	F-CO·H	F-CH : CH$_2$	F-CH : CH·COOC$_2$H$_5$	F-C : N
	170 233 335 395 493	191 336 427 552	162 213 302 503	 217 368 481	 462	183 (311) 570
ω_1	602 618		598 630	655	635	591 640 655
	770 798	785 824	749 775	716 (736) (811)	768 794 862	761 837
ω_2	888	887	882	885	887	887
ω_3	911 922	950	 928 945	908 925	939	 928 938
ω_4	1019	1025	1019	1002 1017 1027	1021	1020
ω_5	1081	1084	1080	1079	1081	1072
ω_6	1122 1172	1163	1151 1159	1145	1160	1151
ω_7	1236	1232	1207 1223	1216	1212	1232
	1307	1254 ?	(1275) ?	1256 1292	1265 1283	
ω_8	1390	1388	1368 1393	1387	1392	1379
			1441			1456
ω_9	1478	1460	1463 1475	1491	1479	1471
ω_{10}	1572 1583	1560	1483 1568	1576	1575	1566
	1726	1744 1777	1668 1688	1642	1640 1704	 2233

Table 5. ω_9 and ω_{10} in α-Mono-derivatives of Furane. (F : )

F–H	1483[13]	
F–CH_3	1510	1605
F–$CH_2CH_2COCH_3$	1509	1597
F–CH_2OH	1507	1602
F–CH_2OCH_3	1501	1593
F–$CH_2OC_2H_5$	1501	1594
F–CH_2OCOCH_3	1505	1604

F–CH : CH_2	1491	1576
F–CH : CH·COOH	1483	1577
F–CH : CH·$COOC_2H_5$	1480	1575
F–CO·OR	1478	1572
F–CO·H	1463 1475	1568
F–CO·Cl	1460	1560
F–C ⋮ N	1471	1566

Table 6.

Molecule	ω_9	ω_{10}
α-Methyl-furane, F–CH_3	1510	1605
α-Furyl-ethylene, F–CH : CH_2	1491	1576
α-Furyl cyanide, F–C ⋮ N	1471	1566

Table 7.

Molecule	ω_9	ω_{10}	Molecule	ω_9	ω_{10}
VII	1503 (1)	1574 (8)	F–CH_3	1510 (10)	1605 (6)
VI	1521 (10)	1590 (6)	F–CHO	1475 (10)	1568 (8)
VIII	1523 (10)	1600 (6)	V	1471 (10)	1566 (6)

As shown in Tables 6 and 7, by comparing ω_9 and ω_{10} in α-mono-derivatives of furane with those in the corresponding α, α'-di-derivatives, the following contrasts are pointed out:

(1) In contrast to the α-mono-derivatives mentioned above, two frequencies corresponding to ω_9 and ω_{10}, are argumented in passing from 2, 5-dimethyl-furane to 2-methyl-furfural-(5) and 2-methyl-furyl cyanide-(5).

(2) The relation of the relative intensities of ω_9 and ω_{10} in α-methy-furane contrasts that in α, α'-dimethyl-furane, while that of ω_9 and ω_{10} in α-furfural and α-furyl cyanide is similar to those in 2-methyl-furfural-(5) and 2-methyl-furyl cyanide-(5), respectively.

(13) G. B. Bonino and R. Manzoni-Ansidei, *Z. physik. Chem.*, B, **25** (1934), 327.

(3) The values of ω_9 and ω_{10} in α-methyl-furane are slightly higher than those in α, α'-dimethyl furane, while those in α-furfural and α-furyl cyanide are lower than those in 2-methyl-furfural-(5) and 2-methyl-furyl cyanide-(5) by about 50 cm.$^{-1}$

In the case of ethyl 2-methyl-furoate-(3), the Raman lines in question, are found at ω_9 1522 and ω_{10} 1608 cm.$^{-1}$, which may be compared with ω_9 1510 and ω_{10} 1605 in α-methyl-furane and ω_9 1478, ω_{10} 1572 cm.$^{-1}$ in α-furoates. It leads to the conclusion that ω_9 and ω_{10} of 2-methyl-furoate-(3) approach nearer to the values of α-methyl-furane than to those of α-furoates, F–COOR.

In α-furyl-ethylene the Raman lines at $\Delta\nu$ 1642 and 1292 cm.$^{-1}$ are associated with the ethylene linkage of the side chain. The latter may correspond to $\Delta\nu$ 1342 cm.$^{-1}$ in ethylene. The weak lines at $\Delta\nu$ 1507 and 1570 cm.$^{-1}$ in 2-methyl-furyl cyanide-(5) may be attributed to 2-furfuryl cyanide, which is possibly expected from the preparation of the sample from α-furfuryl chloride.

The intense lines at $\Delta\nu$ 183(8), 570(8s) and 2233(10) in α-furyl cyanide, may be associated with the structure of R–C≡N, corresponding to $\Delta\nu$ 170(8b), 549(5) and 2224(12b) in phenyl cyanide, and 376(4), 917(3) and 2250(6) in methyl cyanide.

R–C≡N	ω_1	ω_2	ω_3
CH_3–C≡N	2250 (6)	917 (3)	376 (4)
F–C≡N	2233 (10)	570 (8s)	183 (8)
C_6H_5–C≡N	2224 (12b)	549 (5)	170 (8b)

This estimation is made from the relation of the relative intensities and from the order of the mass of R, when we take R for furyl and phenyl in place of methyl radical.

Summary.

(1) The Raman spectra of the following substances have been measured: α-furfuryl methyl ether, α-furfuryl ethyl ether, α-furfuryl-acetone, α-furyl-ethylene, α-furyl cyanide, 2,5-dimethyl-furane, 2-methyl-furyl cyanide-(5) and ethyl 2-methyl-furoate-(3).

(2) The characteristic frequencies of the α-furfuryl-radical are confirmed. The difference of the Raman spectra of the mono- and di-derivatives of furane is established.

(3) The constitutive influences exerted on the Raman frequencies in the region between $\Delta\nu$ 1400 and 1600 cm.$^{-1}$ are observed.

(4) The Raman lines at 1642 and 1292 cm.$^{-1}$ in α-furyl-ethylene are associated with the structure of R–CH : CH_2, and those at 183, 570, and 2233 cm.$^{-1}$ in α-furyl cyanide with the structure of R–C≡N, when R is taken as furyl radical.

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Laboratory of Physical and Inorganic Chemistry,
Taihoku Imperial University, Taihoku.