# STUDIES OF THE RAMAN EFFECT OF ORGANIC SUBSTANCES. PART III. RAMAN EFFECT OF α-MONO-DERIVATIVES OF FURAN.

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## Introduction.

As to the Raman effect of hetero-cyclic compounds with five-membered rings, comparatively few papers have been published. Thiophene and pyrrole have been recently studied by S. Venkateswaran,[1] pyrrole and its derivatives by G. B. Bonino,[2] and some oxydiazole derivatives by M. Milone.[3] The present authors have investigated the Raman effect of furan derivatives in order to find the characteristic Raman lines associated with the furan ring, to find the influences exerted by the groups attached to it, and to confirm the molecular constitution of the furan ring. Ten α-mono-derivatives of furan, viz., α-methyl-furan, α-furfuryl alcohol, α-furfuryl acetate, α-furfural, α-furoyl chloride, methyl α-furoate, ethyl α-furoate, α-furfuracrylic acid, ethyl α-furfuracrylate, and tetrahydro-α-furfuryl alcohol, were examined and the results are reported in the present paper. Furfural has been re-examined to compare the results with the data obtained by K.W.F. Kohlrausch and his co-workers[4] and other authors.[5]

## Experimental.

A spectrograph with three prisms, constructed in our laboratory, was used in the present experiments. The dispersion obtained was 10 Å. per mm. at 4000 Å. and 20 Å. per mm. at 5000 Å., and the experiments were carried out over the range between these extremities. Most of the materials used have been synthesized in our laboratory.

(1) S. Venkateswaren, *Indian J. Phys.*, **5** (1930), 145; **7** (1933), 585.

(2) G. B. Bonino, R. Manzoni-Ansidei, and P. Pratesi, *Z. physik. Chem.*, (B), **22** (1933), 21–44.

(3) M. Milone, *Gazz. chim. ital.*, **63** (1933), 334; **63** (1933), 456.

(4) K.W.F. Kohlrausch, A. Pongratz, and R. Seka, *Ber.*, (B) **66** (1933), 11.

(5) S.S. Lu, ibid.; *Sc. Rep. Nat. Tsing Hua Univ.*, **1** (1931), 25; George Glockler and B. Wiener, *J. Chem. Phys.*, **2** (1934), 47.

α-Methyl-furan(6) (b. p. 64°C.) was prepared by Wolff-Kischner's method, that is, by dropping a small piece of potassium hydroxide into a mixture of furfural, hydrazine hydrate, and methyl alcohol, under sufficient cooling (−30°C.). The substance obtained was washed with a saturated aqueous solution of calcium chloride, dehydrated over calcium chloride, and then redistilled over metallic sodium under the normal pressure.

α-Furfuryl acetate(7) (b.p. 65°/5 mm.) was prepared from α-furfuryl alcohol and acetic anhydride in the presence of fused sodium acetate.

α-Furoyl chloride (b.p. 78°/30 mm.) was made by warming α-furoic acid with thionyl chloride.

Methyl α-furoate (b.p. 57°/5 mm.) and ethyl α-furoate (m.p. 34°, b.p. 78°/8 mm.) were made from α-furoyl chloride with absolute methyl and ethyl alcohols respectively, in the presence of pyridine.

A benzene solution of ethyl α-furoate ($^1/_{10}$ mol) was used for the experiment, as the substance is solid at ordinary temperature.

α-Furfuracrylic acid(8) (m.p. 141°C.) was synthesized from furfural, acetic anhydride, and fused sodium acetate (Perkin's method). The recrystallized substance was dissolved in alcohol ($^1/_{15}$ mol) and used for the experiment of Raman spectra.

Ethyl α-furfuracrylate (b.p. 100°/5 mm.) was prepared by warming a mixture of the silver salt of α-furfuracrylic acid and methyl iodide.

Commercial pure α-furfuryl alcohol and tetrahydro-α-furfuryl alcohol made by Takeda, and furfural made by Merck, were used. All the liquid substances were purified by repeated vacuum distillation after washing and dehydrating.

The results are shown in the accompanying tables I—X and graphically in Fig. 1. In Table A, indices to tables and plates, the numbers of the Raman lines, and the conditions under which the spectra were taken are given for each substance.

About 10 c.c. of each substance was used. In the case of tetrahydro-α-furfuryl alcohol, the observation of the Raman lines was difficult, for most of the lines were so diffuse and broad that an accurate measurement was impossible. During the exposure under the mercury light for two or three hours, α-furfuryl alcohol, furfural, α-furoyl chloride, α-furfuracrylic acid, and its ethyl ester were coloured in faint yellow or brown, so that a redistilled, fresh substance was necessary to continue the exposure for a sufficient time. Even so, most of the lines in the range shorter than 4358

(6) Tadeus Reichstein, *Helvetica Chim. Acta,* **13** (1930), 345; Wolff-Kischner, *Ann.,* **394** (1912), 86.

(7) L. von Wiessel and B. Tollens, *Ann.,* **272** (1893), 303.

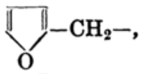
(8) Adolf Baeyer, *Ber.,* **10** (1877), 357.

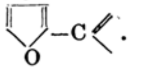
Å. could not be well observed on account of the colouration. By using a saturated solution of sodium nitrite as a filter the back ground of the plates was removed.

The results on furfural obtained by W.K.F. Kohlrausch,[9] S. S. Lu,[10] and G. Glockler and B. Wiener[11] are compared with ours in Table B.

## Discussion of the Results.

The Raman lines corresponding to the frequencies of $\Delta\nu$, 888, 925, 1020, 1081, 1153, 1232, 1390, 3122, and 3153 cm.$^{-1}$, appear intense in all the $\alpha$-derivatives of furan, which may be considered as the characteristic lines of these substances. The weak Raman lines in the region between $\Delta\nu$, 625 and 650 cm.$^{-1}$, and the intense lines of $\Delta\nu$, 888, 1088, and 1390 cm.$^{-1}$, were observed also in thiophene, and pyrrole and its derivatives, though they were not observed in such good constancy as in the case of $\alpha$-derivatives of furan.

The lines in the region between $\Delta\nu$, 1460 and 1605 cm.$^{-1}$, seem to be note-worthy in the case of furan derivatives as well as pyrrole derivatives. In $\alpha$-methyl-furan, $\alpha$-furfuryl alcohol, and $\alpha$-furfuryl acetate, two intense lines of $\Delta\nu$, 1507 and 1605 cm.$^{-1}$, are observed, while in methyl $\alpha$-furoate, ethyl $\alpha$-furoate, ethyl $\alpha$-furfuracrylate, and $\alpha$-furfuracrylic acid, two lines of $\Delta\nu$, 1477 and 1572 cm.$^{-1}$, are observed. From these facts, it is considered that the frequencies of 1507 and 1605 cm.$^{-1}$ can be attributed to the type of 

, while the frequencies of 1477 and 1572 cm.$^{-1}$, to the tye of 

. The high frequency of 1641 cm.$^{-1}$ in furfuracrylic acid and its ethyl ester seems to be attributable to the —CH : CH— linkage in the side chain. In the study of pyrrole and its derivatives, G.B. Bonino and his co-worker[12] have reported that the frequencies of $\Delta\nu$, 1136 and 1466 cm.$^{-1}$, are attributed to the vibration between the two carbon-atoms in $\beta$- and $\beta'$-positions and CH-groups in $\alpha$- and $\alpha'$-positions of the pyrrole ring, respectively. And they have considered that the frequency of 1550 cm.$^{-1}$ is associated with the central vibration, giving a formula of pyrrole like the following :

(9) Cf. (4).
(10) S. S. Lu, *Sc. Rep. Nat. Tsing Hua Univ.*, **1**, (1931), 25.
(11) G. Glockler and B. Wiener, *J. Chem. Phys.*, **2** (1934), 47.
(12) G. B. Bonino and his co-worker, *Z. physik. Chem.*, (B) **22** (1933), 42.

## Table A.

| Substance | No. of Table | No. of Raman lines | No. of Plate | Width of slit ($10^{-2}$ mm.) | Electric current (amp.) | Temperature (C.) | Time of exposure (hours) |
|---|---|---|---|---|---|---|---|
| α-Methyl-furan | I | 53 | 148 | 80 | 4.0 | 20 | 5 |
| | | | 149 | 72 | 4.2 | 20 | 12 |
| | | | 171 | 70 | 4.0 | 15 | 8 |
| | | | 186 | 64 | 4.2 | 19 | 15 |
| α-Furfuryl alcohol | II | 39 | 128 | 90 | 3.5 | 24 | 7 |
| | | | 168 | 64 | 4.0 | 15 | 10 |
| | | | 206 | 70 | 3.8 | 22 | 16 |
| α-Furfuryl acetate | III | 40 | 179 | 70 | 4.0 | 19 | 7 |
| | | | 182 | 64 | 4.0 | 19 | 5 |
| | | | 193 | 70 | 4.0 | 19 | 10 |
| | | | 194 | 80 | 4.0 | 19 | 8 |
| α-Furfural | IV | 54 | 195 | 76 | 4.2 | 20 | 6 |
| | | | 198 | 64 | 4.2 | 20 | 8 |
| | | | 202 | 64 | 4.0 | 21 | 10 |
| α-Furoyl chloride | V | 29 | 178 | 70 | 4.0 | 19 | 5 |
| Methyl α-furoate | VI | 55 | 146 | 90 | 3.8 | 21 | 6 |
| | | | 199 | 70 | 4.2 | 20 | 10 |
| | | | 209 | 64 | 3.8 | 22 | 15 |
| Ethyl α-furoate (in benzene) | VII | 59 | 207 | 70 | 3.8 | 22 | 10 |
| | | | 208 | 64 | 3.8 | 22 | 16 |
| α-Furfuracrylic acid (in alcohol) | VIII | | 139 | 80 | 4.0 | 25 | 14 |
| | | | 200 | 76 | 4.2 | 21 | 12 |
| | | | 201 | 70 | 4.0 | 21 | 16 |
| Ethyl α-furfuracrylate | IX | 36 | 184 | 70 | 4.0 | 20 | 6 |
| | | | 197 | 70 | 4.0 | 20 | 7 |
| | | | 212 | 64 | 4.0 | 23 | 12 |
| | | | 213 | 76 | 4.0 | 23 | 16 |
| Tetrahydro-α-furfuryl alcohol | X | | 169 | 64 | 4.0 | 15 | 8 |
| | | | 170 | 70 | 4.0 | 15 | 7 |
| | | | 190 | 76 | 4.0 | 20 | 12 |

## Table B. Comparison of the results on furfural.

| Lu | Kohlrausch | Glockler | Matsuno and Han |
|---|---|---|---|
| — | — | 172 | 162 (4, *b*, *d*) |
| 282 (1) | — | — | 213 (3) |
| 493 (1) | 501 (3) | 497 | 503 (7) |
| — | — | 581 | 598 (2) |
| — | — | 624 | 630 (2) |
| — | — | 758 | 749 (3*d*)<br>775 (1*d*) |
| — | 881 (3) | 878 | 882 (7*s*) |
| — | 928 (3) | 929 | 928 (8*s*) |
| — | — | — | 946 (4) |
| — | 1018 (5) | 1021 | 1019 (8) |
| — | 1076 (3) | 1078 | 1080 (7) |
| — | 1147 (5) | 1156 | 1151 (6)<br>1159 (7) |
| — | 1212 (2) | — | |
| — | — | 1221 | 1207 (1)<br>1223 (4*d*) |
| — | — | — | (1275) (2) |
| 1369 (7) | 1359 (10) | 1378 | 1368 (10) |
| — | 1384 (8) | | 1393 (10) |
| — | — | — | 1441 (2) |
| 1461 (7) | 1461 (15) | 1467 | 1463 (10)<br>1475 (10) |
| — | — | — | 1484 (1) |
| 1500 (2) | 1561 (4) | 1567 | 1568 (8) |
| 1662 (3) | 1665 (15)<br>1683 (10) | 1677 | 1668 (10*b*)<br>1688 (8, *b*, *d*) |
| — | | 2881 | (3123) (4) |
| 2998 (3) | | 3129 | (3151) (2) |

## Table I.

### α-Methyl-furan, $C_4H_3O{\cdot}CH_3$.

| No. | ν (cm.⁻¹) | *I* | ν₀—Δν | No. | ν (cm.⁻¹) | *I* | ν₀—Δν |
|---|---|---|---|---|---|---|---|
| 1 | 24463 | 4 (*d*) | *q*-2925 (*k*-242) | 28 | 22049 | 3 | *e*-889 |
| 2 | 24426 | 2 (*d*) | *q*-2962 (*p*-2927) | 29 | 22021 | 4 | *e*-917 |
| 3 | 24365 | 1 (*d*) | *k*-340 | 30 | 21962 | 2 | *k*-2743 (*e*-976) ? |
| 4 | 24270 | 1 (*d*) | *q*-3118 | 31 | 21920 | 3 | *e*-1018 |
| 5 | 24235 | 1 (*d*) | *q*-3153 (*p*-3118) | 32 | 21854 | 8 (*s*) | *e*-1084 |
| 6 | 24078 | 1 | *k*-627 | 33 | 21816 | 3 | *k*-2889 |
| 7 | 24052 | 2 | *k*-653 | 34 | 21791 | 3 | *e*-1147 |
| 8 | 23818 | 1/2 | *k*-887 | 35 | 21776 | 7 | *k*-2929 |
| 9 | 23787 | 1 | *k*-918 | 36 | 21751 | 2 (*d*) | *k*-2954 |
| 10 | 23687 | 1/2 (*d*) | *k*-1018 | 37 | 21723 | 4 | *e*-1215 |
| 11 | 23621 | 6 (*s*) | *k*-1084 | 38 | 21705 | 3 | *e*-1233 (*k*-3000)? |
| 12 | 23558 | 2 (*d*) | *k*-1147 | 39 | 21586 | 6 (*d*) | *k*-3119 |
| 13 | 23490 | 2 | *k*-1215 | 40 | 21562 | 3 (*d*) | *e*-1376 |
| 14 | 23471 | 1 | *k*-1234 | 41 | 21549 | 6 (*d*) | *e*-1389 (*k*-3156) |
| 15 | 23436? | 1/2 | *i*-1080 | 42 | 21486 | 4 (*d*) | *e*-1452 (*f*-1509) |
| 16 | 23329 | 3 | *k*-1376 | 43 | 21428 | 10 | *e*-1510 |
| 17 | 23316 | 3 | *k*-1389 | 44 | 21394 | 1 | *i*-3122 (*f*-1601) |
| 18 | 23251 | 4 | *k*-1454 | 45 | 21363 | 1 | *i*-3153 |
| 19 | 23194 | 8 | *k*-1511 | 46 | 21334 | 6 | *e*-1604 |
| 20 | 23100 | 5 | *k*-1605 | 47 | 20191 | 1 | *e*-2747 |
| 21 | 22685 | 5 (*d*) | *e*-253 | 48 | 20051 | 1 | *e*-2887 |
| 22 | 22595 | 3 (*d*) | *e*-343 | 49 | 20010 | 5 | *e*-2928 |
| 23 | 22312 | 3 | *e*-626 | 50 | 19982 | 1 | *e*-2956 |
| 24 | 22284 | 6 | *e*-654 | 51 | 19937? | 1/2 | *e*-3001 |
| 25 | 22220 | 1 (*b*, *d*) | *e*-718 | 52 | 19815 | 3 | *e*-3123 |
| 26 | 22142 | 1 (*d*) | *e*-796 | 53 | 19785 | 2 | *e*-3153 |
| 27 | 22083 | 1 (*d*) | *e*-855 (*f*-912) | | | | |

Δν: 253 (5*d*); 343 (3*d*); 626 (3); 654 (6); 718 (1*b*, *d*); 796 (1*d*); (855) (1*d*); 888 (3); 917 (4); (976) (2)?; 1018 (3); 1084 (8*s*); 1147 (3); 1215 (4); 1233 (3); 1376 (3); 1389 (6*d*): 1453 (4*d*); 1510 (10); 1605 (6); 2745 (2); 2888 (3); 2928 (7); 2955 (2*d*); 3000 (1)?; 3119 (6*d*); 3153 (4*d*).

## Table II.

### α-Furfuryl alcohol, $C_4H_3O{\cdot}CH_2OH$.

| No. | $\nu$ (cm.$^{-1}$) | $I$ | $\nu_0-\Delta\nu$ | No. | $\nu$ (cm.$^{-1}$) | $I$ | $\nu_0-\Delta\nu$ |
|---|---|---|---|---|---|---|---|
| 1 | 23816 | 1/2 | *k*-889 | 21 | 21979 | 1/2 | *e*-959 |
| 2 | 23783 | 0 | *k*-922 | 22 | 21920 | 2 (*b*, *d*) | *e*-1018 |
| 3 | 23687 | 1/2 (*d*) | *k*-1018 | 23 | 21855 | 6 | *e*-1083 |
| 4 | 23623 | 2 | *k*-1082 | 24 | 21825 | 1 (*d*) | *k*-2880 |
| 5 | 23552 | 1 (*d*) | *k*-1153 | 25 | 21784 | 3 (*d*) | *e*-1154 |
| 6 | 23478 | 2 | *k*-1227 | 26 | 21710 | 4 | *e*-1228 |
| 7 | 23440 | 1/2 (*d*) | *k*-1265 | 27 | 21669 | 1 (*d*) | *e*-1269 |
| 8 | 23328 | 1 (*d*) | *k*-1377 | 28 | 21587 | 4 (*d*) | *k*-3118 |
| 9 | 23312 | 2 (*d*) | *k*-1393 | 29 | 21567 | 1 | *e*-1371 |
| 10 | 23225 | 1 (*bb*) | *k*-1480 | 30 | 21548 | 4 (*d*) | *e*-1390 (*k*-3157) |
| 11 | 23198 | 6 | *k*-1507 | 31 | 21463 | 2 (*b*, *d*) | *e*-1475 |
| 12 | 23104 | 4 | *k*-1601 | 32 | 21431 | 8 | *e*-1507 |
| 13 | 22761 | 4 (*d*) | *e*-177 | 33 | 21396 | 1 | *i*-3120 |
| 14 | 22517 | 1 (*b*, *d*) | *e*-421 | 34 | 21363 | 1 (*d*) | *i*-3153 |
| 15 | 22335 | 1/2 (*d*) | *e*-603 | 35 | 21336 | 4 (*d*) | *e*-1602 |
| 16 | 22312 | 2 (*d*) | *e*-626 | 36 | 21066 | 1 (*d*) | *e*-2872 |
| 17 | 22197 ? | 0 (*d*) | *e*-741 | 37 | 19998 | 2 (*b*, *d*) | *e*-2940 |
| 18 | 22122 ? | 0 (*d*) | *e*-816 | 38 | 19821 | 4 | *e*-3117 |
| 19 | 22051 | 3 | *e*-887 | 39 | 19787 | 3 | *e*-3151 |
| 20 | 22016 | 2 | *e*-922 | | | | |

$\Delta\nu$: 177 (4*d*); 421 (1*b*, *d*); 603 (1/2); 626 (2*d*); 741 (0*d*)?; 816 (1/2*d*); 888 (3); 922 (2); 959 (1/2); 1018 (2*b*, *d*); 1083 (6); 1154 (3*d*); 1228 (4); 1267 (1*d*) 1374 (1); 1391 (4*d*); 1477 (2*b*, *d*): 1507 (8); 1602 (4*d*), 2876 (1*d*); 2940 (2*b*, *d*)?; 3117 (4); 3154 (3).

## Table III.

### $\alpha$-Furfuryl acetate, $C_4H_3O \cdot CH_2O \cdot OC \cdot CH_3$.

| No. | $\nu$ (cm.$^{-1}$) | $I$ | $\nu_0 - \Delta\nu$ |
|---|---|---|---|
| | 24046 | ½ (*d*) | *k*-659 |
| 2 | 23821 | 1 | *k*-884 |
| 3 | 23782 | 2 (*d*) | *k*-923 |
| 4 | 23738 | 0 (*d*) | *k*-967 |
| 5 | 23683 | 2 (*d*) | *k*-1022 |
| 6 | 23623 | 3 | *k*-1082 |
| 7 | 23581 | 1(*b*, *d*) | *k*-1124 (*i*-935) |
| 8 | 23553 | 3 (*d*) | *k*-1152 |
| 9 | 23473 | 2 (*d*) | *k*-1232 |
| 10 | 23439 | ½ (*d*) | *i*-1077 |
| 11 | 23320 | 3 | *k*-1385 |
| 12 | 23199 | 6 | *k*-1506 |
| 13 | 23129 | 1 (*d*) | *i*-1387 |
| 14 | 23102 | 4 | *k*-1603 |
| 15 | 22766 ? | ½ (*d*) | *e*-172 |
| 16 | 22745 ? | 1 (*d*) | *e*-193 |
| 17 | 22623 ? | ½ (*d*) | *e*-315 |
| 18 | 22606 | ½ (*d*) | *e*-332 |
| 19 | 22317 | 3 (*d*) | *e*-621 |
| 20 | 22279 | 4 | *e*-659 |
| 21 | 22193 | 1 (*d*) | *e* 745 |
| 22 | 22103 | 1(*b*, *d*) | *e*-835 (*f*-892) |
| 23 | 22052 | 5 | *e*-886 |
| 24 | 22013 | 4 | *e*-925 |
| 25 | 21974 | 1 | *e*-964 |
| 26 | 21916 | 4 | *e*-1022 |
| 27 | 21855 | 6 | *e*-1083 |
| 28 | 21784 | 1 | *e*-1154 |
| 29 | 21759 | 4 | *k*-2946 |
| 30 | 21708 | 3 | *e*-1230 |
| 31 | 21577 | 6 (*d*) | *k*-3128 |
| 32 | 21545 | 6 (*d*) | *e*-1393 (*k*-3160) |
| 33 | 21488 | 2 (*d*) | *e*-1450 (*f*-1507) |
| 34 | 21434 | 8 | *e*-1504 |
| 35 | 21393 | ½ | *i*-3123 (*f*-1602) |
| 36 | 21333 | 6 | *e*-1605 |
| 37 | 21193 | 2 (*d*) | *e*-1745 |
| 38 | 19993 | 4 | *e*-2945 |
| 39 | 19809 | 4 | *e*-3131 |
| 40 | 19782 | 2 (*d*) | *e*-3156 |

$\Delta\nu$: 172 (½*d*)? ; 193 (½*d*)? ; 315 (½*d*)? ; 332 (½) ; 621 (3*d*) ; 659 ; 659 (4) ; 745 (1*d*)? ; 835 (1*b*, *d*)? ; 886 (5) ; 924 (4) ; 964 (1) ; 1022 (4) ; 1083 (6) ; 1153 (1) ; 1231 (3) ; 1389 (6*d*) ; 1450 (2*d*) ; 1505 (8) ; 1604 (6) ; 1745 (3*d*) ; 2946 (4) ; 3130 (6*d*) ; 3156 (3).

## Table IV.

### α-Furfural, $C_4H_3O \cdot CO \cdot H$.

| No. | $\nu$ (cm.$^{-1}$) | $I$ | $\nu_0 - \Delta\nu$ | No. | $\nu$ (cm.$^{-1}$) | $I$ | $\nu_0 - \Delta\nu$ |
|---|---|---|---|---|---|---|---|
| 1 | 24203 | 2 | *k*-502 | 28 | 22189 | 3 (*d*) | *e*-749 |
| 2 | 23822 | 2 | *k*-883 | 29 | 22163 | 1 (*d*) | *e*-775 |
| 3 | 23774 | 3 | *k*-931 | 30 | 22056 | 7 (*s*) | *e*-882 |
| 4 | 23760 | 1 | *k*-945 | 31 | 22012 | 8 (*s*) | *e*-926 |
| 5 | 23687 | 4 | *k*-1018 | 32 | 21992 | 4 | *e*-946 |
| 6 | 23625 | 2 (*d*) | *k*-1080 | 33 | 21918 | 8 | *e*-1020 |
| 7 | 23550 | 3 (*d*) | *k*-1155 | 34 | 21858 | 7 | *e*-1080 |
| 8 | 23500 | 1/2 | *k*-1205 | 35 | 21787 | 6 | *e*-1151 |
| 9 | 23443 ? | 0 | *i*-1073 | 36 | 21779 | 7 | *e*-1159 |
| 10 | 23357 | 0 | *i*-1159 | 37 | 21729 | 0 | *e*-1209 |
| 11 | 23338 | 7 | *k*-1367 | 38 | 21715 | 4 (*d*) | *e*-1223 |
| 12 | 23312 | 7 | *k*-1393 | 39 | 21663 | 2 | *e*-1275 |
| 13 | 23262 | 1/2 | *k*-1443 | 40 | 21625 | 2 | *f*-1370 |
| 14 | 23241 | 8 | *k*-1464 | 41 | 21601 | 3 | *f*-1394 |
| 15 | 23229 | 8 | *k*-1476 | 42 | 21570 | 10 | *e*-1368 |
| 16 | 23220 | 1 | *k*-1485 | 43 | 21545 | 10 | *e*-1393 |
| 17 | 23149 | 2 | *i*-1367 | 44 | 21498 | 2 | *e*-1440 |
| 18 | 23136 | 4 | *k*-1569 | 45 | 21476 | 10 | *e*-1462 |
| 19 | 23122 | 2 | *i*-1394 | 46 | 21465 | 10 | *e*-1473 |
| 20 | 23054 | 1 | *i*-1462 | 47 | 21456 | 1 | *e*-1482 |
| 21 | 22832 | 3 (*b*, *d*) | *f*-163 | 48 | 21371 | 8 | *e*-1567 |
| 22 | 22776 | 4 (*b*, *d*) | *e*-162 | 49 | 21323 | 2 | *f*-1672 |
| 23 | 22725 | 3 | *e*-213 | 50 | 21297 | 2 | *f*-1698 |
| 24 | 22636 | 1/2 | *e*-302 | 51 | 21270 | 10 (*b*) | *e*-1668 |
| 25 | 22435 | 7 | *e*-503 | 52 | 21250 | 8 (*b*, *d*) | *e*-1688 |
| 26 | 22340 | 2 | *e*-598 | 53 | 19815 | 4 | *e*-1523 |
| 27 | 22308 | 2 | *e*-630 | 54 | 19787 | 2 | *e*-3151 |

$\Delta\nu$; 162 (4, *b*, *d*); 213 (3); 302 (1/2); 503 (7); 598 (2); 630 (2); 749 (3*d*); 775 (1*d*); 882 (7*s*); 928 (8*s*); 946 (4). 1019 (8); 1080 (7); 1151 (6); 1159 (7); 1207 (1); 1223 (4*d*); (1275) (2); 1368 (10); 1393 (10); 1441 (2); 1463 (10); 1475 (10); 1483 (1); 1568 (8): 1668 (10*b*); 1688 (8, *b*, *d*); (3123) (4); (3151) (2).

Table V. Furoyl chloride, $C_4H_3O\cdot CO\cdot Cl$.

| No. | $\nu$ (cm.$^{-1}$) | $I$ | $\nu_0-\Delta\nu$ | No. | $\nu$ (cm.$^{-1}$) | $I$ | $\nu_0-\Delta\nu$ |
|---|---|---|---|---|---|---|---|
| 1 | 23682 | 1/2 | *k*-1023 | 16 | 22051 | 4 | *e*-887 |
| 2 | 23626 | 1/2 | *k*-1079 | 17 | 21988 | 4 | *e*-950 |
| 3 | 23541 | 2 | *k*-1164 | 18 | 21910 | 5 (*d*) | *e*-1028 |
| 4 | 23490 | 0 (*d*) | *i*-1026 | 19 | 21854 | 5 | *e*-1084 |
| 5 | 23318 | 5 | *k*-1387 | 20 | 21775 | 5 (*d*) | *e*-1163 |
| 6 | 23245 | 8 (*b*, *d*) | *k*-1460 | 21 | 21706 | 3 | *e*-1232 |
| 7 | 23146 | 2 (*s*) | *k*-1559 | 22 | 21684 ? | 1/2 | *e*-1254 |
| 8 | 23127 | 2 (*d*) | *i*-1389 | 23 | 21576 | 1 (*b*, *d*) | *k*-3129 |
| 9 | 23053 | 2 | *i*-1463 | 24 | 21549 | 8 (*d*) | *e*-1389 (*k*-3156) |
| 10 | 22747 | 4 (*b*, *d*) | *e*-191 (*i*-1769) | 25 | 21479 | 10 (*d*) | *e*-1459 |
| 11 | 22602 | 3 | *e*-336 | 26 | 21377 | 4 | *e*-1561 |
| 12 | 22511 | 4 | *e*-427 | 27 | 21194 | 8 (*b*, *d*) | *e*-1744 |
| 13 | 22386 | 6 | *e*-552 | 28 | 21161 | 4 (*b*, *d*) | *e*-1777 ? |
| 14 | 22153 ? | 1 (*b*, *d*) | *e*-780 | 29 | 19810 | 1/2 (*d*) | *e*-3128 |
| 15 | 22114 | 2 (*b*, *d*) | *e*-824 | | | | |

$\Delta\nu$: 191 (4*b*, *d*); 336 (3); 427 (4); 552 (6); 785 (1*b*, *d*)?; 824 (2*b*, *d*)? 887 (4); 950 (4); 1025 (5*d*); 1084 (5); 1163 (5*d*); 1232 (3); 1254 (1/2)?; 1388 (8*d*); 1460 (10*d*); 1560 (4); 174 (8*b*, *d*); 1777 (4*b*, *d*); 3129 (1*b*, *d*),

Table VI. Methyl $\alpha$-furoate, $C_4H_3O\cdot CO\cdot O\cdot CH_3$.

| No. | $\nu$ (cm.$^{-1}$) | $I$ | $\nu_0-\Delta\nu$ | No. | $\nu$ (cm.$^{-1}$) | $I$ | $\nu_0-\Delta\nu$ |
|---|---|---|---|---|---|---|---|
| 1 | 24468 | 1 | *k*-237 | 13 | 23782 | 4 | *k*-923 |
| 2 | 24426 | 2 | *q*-2962 | 14 | 23687 | 4 (*d*) | *k*-1018 |
| 3 | 24372 | 1/2 (*b*) | *k*-331 | 15 | 28624 | 4 | *k*-1081 (*i*-892) |
| 4 | 24312 | 2 (*d*) | *k*-393 | 16 | 23582 | 4 (*d*) | *k*-1123 |
| 5 | 24259 | 1/2 (*d*) | *q*-3129 | 17 | 23532 | 4 (*b*, *d*) | *k*-1173 |
| 6 | 24227 | 1/2 (*b*, *d*) | *q*-3161 (*p*-3126) | 18 | 23502 | 1 (*b*, *d*) | *i*-1014 |
| 7 | 24092 | 0 | *k*-613 | 19 | 23465 | 3 | *k*-1240 |
| 8 | 24080 | 0 | *k*-625 | 20 | 23443 | 1 (*d*) | *i*-1073 |
| 9 | 23932 | 1/2 | *k*-773 | 21 | 23396 | 2 (*d*) | *k*-1309 (*i*-1126) |
| 10 | 23906 | 3 | *k*-799 | 22 | 23314 | 6 (*b*) | *k*-1391 |
| 11 | 23816 | 3 | *k*-889 | 23 | 23227 | 8 (*b*) | *k*-1478 |
| 12 | 23793 | 3 | *k*-912 | | | | |

## Table VI.—(*Concluded*)

| No. | $\nu$ (cm.$^{-1}$) | $I$ | $\nu_0 - \Delta\nu$ | No. | $\nu$ (cm.$^{-1}$) | $I$ | $\nu_0 - \Delta\nu$ |
|---|---|---|---|---|---|---|---|
| 24 | 23131 | 4 | *k*-1574 (*i*-1385) | 41 | 21817 | 5 (*b*, *d*) | *e*-1121 |
| 25 | 23120 | 5 | *k*-1585 | 42 | 21767 | 4 (*b*, *d*) | *e*-1171 |
| 26 | 22792 | 2(*b*, *dd*) | *i*-1724 | 43 | 21747 | 5 (*b*, *d*) | *k*-2958 |
| 27 | 22768 | 2 (*dd*) | *e*-170 (*f*-227) | 44 | 21705 | 5 | *e*-1233 |
| 28 | 22705 | 5 (*b*, *d*) | *e*-233 | 45 | 21632 | 4 | *e*-1306 |
| 29 | 22599 | 1/2 | *e*-339 | 46 | 21582 | 4 | *k*-3123 |
| 30 | 22540 | 4 | *e*-398 | 47 | 21548 | 8 (*b*) | *e*-1390 (*k*-3157) |
| 31 | 22445 | 3 | *e*-493 | 48 | 21460 | 10 (*bb*) | *e*-1478 |
| 32 | 22336 | 1 | *e*-602 | 49 | 21367 | 5 | *e*-1571 |
| 33 | 22320 | 2 (*d*) | *e*-618 | 50 | 21356 | 6 | *e*-1582 |
| 34 | 22172 | 3 (*d*) | *e*-766 | 51 | {21219<br>{21204 | 8 (*b*) | *e*-1719 }<br>*e*-1734 } *e*-1726 |
| 35 | 22141 | 6 | *e*-797 | 52 | 20094 | 1 (*d*) | *e*-2844 |
| 36 | 22051 | 6 | *e*-887 | 53 | 19984 | 4 | *e*-2954 |
| 37 | 22027 | 5 | *e*-911 | 54 | 19817 | 4 | *e*-3121 |
| 38 | 22016 | 8 | *e*-922 | 55 | 19784 | 2 (*d*) | *e*-3154 |
| 39 | 21919 | 6 (*d*) | *e*-1019 | | | | |
| 40 | 21858 | 6 (*d*) | *e*-1080 (*k*-2847) | | | | |

$\Delta\nu$ : 170 (2*dd*) ; 233 (5*bb*) ; 335 (1/2) ; 395 (4) ; 493 (3) ; 602 (1) ; 618 (2*d*) ; 770 (3*d*) ; 798 (6); 888 (6) ; 911 (5) ; 922 (8) : 1019 (6*d*) ; 1081 (6*d*) ; 1122 (5*b*, *d*) ; 1172 (4*b*, *d*) ; 1236 (5) ; 1307 (4) ; 1390 (8*b*) ; 1478 (10*bb*) ; 1572 (5) ; 1583 (6) ; 1726 (8*bb*) ; 2845 (1*d*) ; 2956 (5*b*, *d*) ; 3122 (4) ; 3155 (2*d*).

## Table VII. Ethyl $\alpha$-furoate, $C_4H_3O \cdot CO \cdot O \cdot C_2H_5$ .

| No. | $\nu$ (cm.$^{-1}$) | $I$ | $\nu_0 - \Delta\nu$ | No. | $\nu$ (cm.$^{-1}$) | $I$ | $\nu_0 - \Delta\nu$ |
|---|---|---|---|---|---|---|---|
| 1 | 24336 | 4 | *q*-3052 | 10 | 23722 | 2 | *k*-983 |
| 2 | 24325 | 3 (*d*) | *q*-3063 | 11 | 23714 | 8 | *k*-991 |
| 3 | 24290 | 2 (*d*) | *p*-3063 | 12 | 23628 | 3 (*d*) | *k*-1080 (*i*-888) |
| 4 | 24228 | 2 (*d*) | *p*-3125 (*q*-3160) | 13 | 23582 | 3 (*d*) | *k*-1123 (*i*-934) |
| 5 | 24098 | 3 | *k*-607 | 14 | 23524 | 6 | *k*-1181 (*i*-993) |
| 6 | 23936 | 1 | *k*-769 | 15 | 23474 | 1/2 | *k*-1231 |
| 7 | 23839 ? | 1/2 | *k*-866 | 16 | 23340 | 1 | *i*-1176 |
| 8 | 23817 | 1 | *k*-888 | 17 | 23319 | 3 | *k*-1386 |
| 9 | 23778 | 3 | *k*-927 | | | | |

## Table VII.—(*Concluded*)

| No. | $\nu$ (cm.$^{-1}$) | $I$ | $_0-\Delta\nu$ | No. | $\nu$ (cm.$^{-1}$) | $I$ | $\nu_0-\Delta\nu$ |
|---|---|---|---|---|---|---|---|
| 18 | 23304 | 2 | *k*-1401 | 39 | 21760 | 6 (*d*) | *e*-1178 (*k*-2945) |
| 19 | 23228 | 6 (*b*) | *k*-1477 | 40 | 21725 | ½ | *k*-2980 |
| 20 | 23134 | 1 | *k*-1571 | 41 | 21706 | 2 | *e*-1232 |
| 21 | 23123 | 4 (*b*) | (*i*-1382) *k*-1582 | 42 | 21654 | 6 (*d*) | *k*-3051 |
| 22 | 23100 | 3 (*d*) | *k*-1605 | 43 | 21642 | 8 | *k*-3063 |
| 23 | 22730 | 3 (*b*, *d*) | *e*-208 | 44 | 21582 | 3 (*d*) | *k*-3123 |
| 24 | 22585 | 3 | *e*-353 | 45 | 21552 | 6 | *e*-1386 |
| 25 | 22433 | 1 | *e*-505 | 46 | 21541 | 3 | *k*-3164 |
| 26 | 22332 | 6 | *e*-606 | 47 | 21521 | 3 | *k*-3184 |
| 27 | 22251 | ½ | *e*-687 | 48 | 21488 | ½ | *e*-1450 |
| 28 | 22176 | 3 (*d*) | *e*-762 | 49 | 21464 | 8 (*b*) | *e*-1474 |
| 29 | 22088 | 4 | *e*-850 | 50 | 21367 | 1 | *e*-1571 (*i*-3149) |
| 30 | 22078 | 4 | *e*-860 (*f*-917) | 51 | 21355 | 6 (*d*) | *e*-1583 |
| 31 | 22051 | 4 | *e*-887 | 52 | 21333 | 5 | *e*-1605 |
| 32 | 22009 | 5 | *e*-929 | 53 | 21224 | 8 | *e*-1714 |
| 33 | 21956 | 2 | *e*-983 | 54 | 21207 | 8 | *e*-1731 |
| 34 | 21944 | 10 | *e*-994 | 55 | 20011 | ½ | *e*-2927 |
| 35 | 21921 | 1 (*d*) | *e*-1017 | 56 | 19993 | 1 | *e*-2945 |
| 36 | 21859 | 5 | *e*-1079 | 57 | 19889 | 3 | *e*-3049 |
| 37 | 21815 | 4 (*b*, *d*) | *e*-1123 | 58 | 19874 | 6 | *e*-3064 |
| 38 | 21780 | 1 (*d*) | *k*-2925 | 59 | 19816 | 1 | *e*-3122 |

Benzene: 606 (6); (687) (½); 850 (4); 983 (2); 993 (10); 1179 (5); (1401) (2); 1583 (6*d*); 1605 (5); 2945 (1); 3051 (6*d*); 3063 (8); 3164 (3); 3184 (3).

Ethyl α-furoate: 208 (3, *b*, *d*); 353 (3); 505 (1); 606 (?); 765 (3*d*); 860 (4); 887 (4). 928 (5); 1017 (1*d*); 1079 (5); 1123 (4, *b*, *d*); 1179 (?); 1232 (2); 1386 (6); (1401) (2)?; 1450 (½); 1476 (8*b*); 1571 (1): 1583 (6*d*); 1714 (8); 1731 (8); 2926 (1*d*); 2980 (½); 3123 (3*d*).

## Table VIII. α-Furfuracrylic acid, $C_4H_3O\cdot CH:CH\cdot CO\cdot OH$. (in alcohol).

| No. | $\nu$ (cm.$^{-1}$) | $I$ | $\nu_0-\Delta\nu$ | No. | $\nu$ (cm.$^{-1}$) | $I$ | $\nu_0-\Delta\nu$ |
|---|---|---|---|---|---|---|---|
| 1 | 24069 | 0 (*d*) | *k*-636 | 6 | 23682 | 3 | *k*-1023 |
| 2 | 23994 | 1 (*d*) | *k*-711 | 7 | 23622 | ½ (*d*) | *k*-1083 |
| 3 | 23930 | 2 | *k*-775 | 8 | 23551 | ½(*b*, *d*) | *k*-1154 |
| 4 | 23818 | 2 | *k*-887 | 9 | 23430 | 2 (*b*) | *k*-1275 |
| 5 | 23736 | ½ | *k*-697 | 10 | 23309 | 4 | *k*-1396 |

Table VIII.—(*Concluded*)

| No. | ν (cm.⁻¹) | I | ν₀—Δν | No. | ν (cm.⁻¹) | I | ν₀—Δν |
|---|---|---|---|---|---|---|---|
| 11 | 23220 | 6 | k-1485 | 24 | 21733 | 4 | k-2972 |
| 12 | 23127 | 2(d) | k-1578 (i-1389) | 25 | 21655 | 4(d) | e-1283 |
| 13 | 23063 | 6(d) | k-1642 | 26 | 21585 | 1 | k-3120 |
| 14 | 22312 | 1/2 | e-626 | 27 | 21551 | 5 | e-1387 |
| 15 | 22169 | 1(d) | e-769 | 28 | 21486 | 1 | e-1452 |
| 16 | 22089 | 0 | e-849 | 29 | 21456 | 8 | e-1482 |
| 17 | 22057 | 5 | e-881 | 30 | 21363 | 1 | e-1575 |
| 18 | 21974 | 1/2 | e-964 | 31 | 21297 | 10 | e-1641 |
| 19 | 21917 | 5 | e-1021 | 32 | 21254 | 2(d) | e-1684 |
| 20 | 21886 | 1/2(d) | e-1052 | 33 | 20060 | 2 | e-2878 |
| 21 | 21853 | 1(d) | e-1085 | 34 | 20015 | 3 | e-2923 |
| 22 | 21825 | 3(d) | k-2880 | 35 | 19967 | 3 | e-2971 |
| 23 | 21781 | 5(d) | e-1157 (k-2924) | 36 | 19815 | 1/2 | e-3123 |

Alcohol: 849 (0); 884 (5); 1052 (1/2*d*); 1084 (1*d*); 1159 (5*d*); 1279 (4*d*); 1452 (1); 2879 (3*d*); 2924 (5*d*); 2972 (4).

α-Furfuracrylic acid: 631 (1/2*d*)?; (711) (1/2*d*)?; 772 (1*d*); 884 (5); 962 (1/2); 1022 (5); 1084; (1*d*); 1156 (5*d*); 1392 (5); 1483 (8); 1577 (2*d*); 1641 (10); 1634 (2*d*); 3121 (1).

Table IX. Ethyl α-furfuracrylate, $C_4H_3O \cdot CH:CH \cdot CO \cdot O \cdot C_2H_5$.

| No. | (ν cm.⁻¹) | I | ν₀—Δν | No. | ν (cm.⁻¹) | I | ν₀—Δν |
|---|---|---|---|---|---|---|---|
| 1 | 23684 | 3 | k-1021 | 14 | 22303? | 0(d) | e-635 |
| 2 | 23622 | 1/2(d) | k.1083 | 15 | 22170 | 2 | e-768 |
| 3 | 23544 | 1(d) | k-1161 | 16 | 22144 | 2 | e-794 |
| 4 | 23492 | 2 | k-1213 | 17 | 22076 | 1/2 | e-862 |
| 5 | 23441 | 2 | k-1264 | 18 | 22051 | 3 | e-887 |
| 6 | 23421 | 3 | k-1284 | 19 | 21999 | 1 | e-939 |
| 7 | 23309 | 5 | k-1396 | 20 | 21917 | 8 | e-1021 |
| 8 | 23225 | 8 | k-1480 | 21 | 21857 | 4 | e-1081 |
| 9 | 23127 | 1 | h-1578 | 22 | 21778 | 5(d) | e-1160 |
| 10 | 23061 | 8 | k-1644 | 23 | 22726 | 5 | e-1212 |
| 11 | 22873 | 4 | i-1643 | 24 | 21673 | 5 | e-1265 |
| 12 | 22806 | 1/2(d) | i-1710 | 25 | 21655 | 8 | e-1283 |
| 13 | 22476 | 1/2 | e-462 | 26 | 21577 | 1 | e-3128 |

Table IX.—(*Concluded*)

| No. | $\nu$ (cm.$^{-1}$) | $I$ | $\nu_0-\Delta\nu$ | No. | $\nu$ (cm.$^{-1}$) | $I$ | $\nu_0-\Delta\nu$ |
|---|---|---|---|---|---|---|---|
| 27 | 21549 | 9 | *e*-1389 (*k*-3156) | 32 | 20010 | 1 (*d*) | *e*-2928 |
| 28 | 21460 | 10 | *e*-1478 | 33 | 19965 | 2 | *e*-2973 |
| 29 | 21367 | 4 | *e*-1571 | 34 | 19900 | 5 | *e*-3038 |
| 30 | 21298 | 10 | *e*-1640 | 35 | 19817 | 2 | *e*-3121 |
| 31 | 21234 | 8 (*d*) | *e*-1704 | 36 | 19787 | 1 (*d*) | *e* 3151 |

$\Delta\nu$: 462 (1/2); 635 (0*d*)?; 768 (2); 794 (2); 862 (1/2); 887 (3); 939 (1); 1021 (8); 1081 (4); 1160 (5*d*); 1212 (6); 1265 (5); 1283 (8); 1392 (9); 1479 (10); 1575 (4); 1640 (10); 1704 (8*b*, *d*); 2926 (1*d*); 2976 (2); 3035 (5); 3125 (2); 3154 (1).

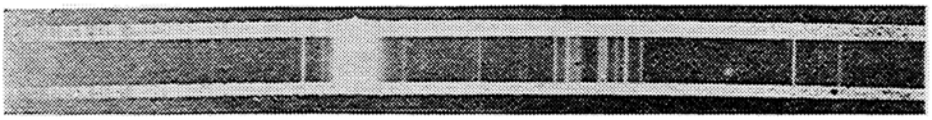
Table X.

Tetrahydro-$\alpha$-furfuryl alcohol, $C_4H_7O{\cdot}CH_2{\cdot}OH$.

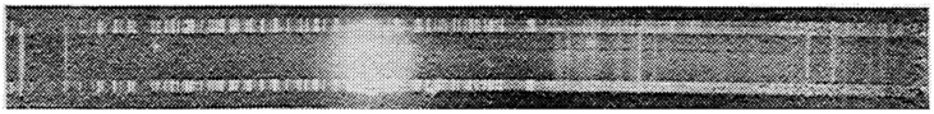
| No. | $\nu$ (cm.$^{-1}$) | $I$ | $\nu_0-\Delta\nu$ | No. | $\nu$ (cm.$^{-1}$) | $I$ | $\nu_0-\Delta\nu$ |
|---|---|---|---|---|---|---|---|
| 1 | 23783 | 4 (*d*) | *k*-922 | 9 | 21931 | 2 (*d*) | *k*-2774 |
| 2 | 23576 | 1/2 (*d*) | *k*-1129 | 10 | 21821 | 6 (*d*) | *e*-1117 |
| 3 | 23251 | 3 (*d*) | *k*-1454 | 11 | {21759 | 4 (*b*, *d*) | {*k*-2946 |
| 4 | 22787 | 2 (*d*) | *e*-151 | 12 | {21728 | 4 (*b*, *d*) | {*k*-2978 |
| 5 | 22766 | 1 (*d*) | *e*-172 | 13 | 21488 | 4 | *e*-1450 |
| 6 | 22121 | 3 (*b*, *d*) | *e*-817 | 14 | 21451 | 3 | *e*-1487 |
| 7 | 22062? | 1/2 (*b*, *d*) | ? | 15 | 20000 | | *e*-2938 |
| 8 | 22023 | 6 (*d*) | *e*-915 | 16 | 19958 | 3 (*b*) | *e*-2980 |

$\Delta\nu$: 151 (2*d*); 172 (1*d*); 817 (3b, *d*); 918 (6*d*); 1123 (6*d*); 1452 (4*d*); 1487 (3*d*); (2774) (2*d*); 2942–2979 (4*b*, *d*).

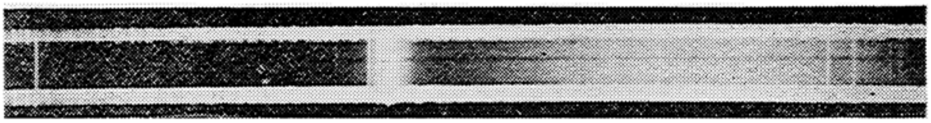
$\alpha$-Methyl-furan $C_4H_3O{\cdot}CH_3$



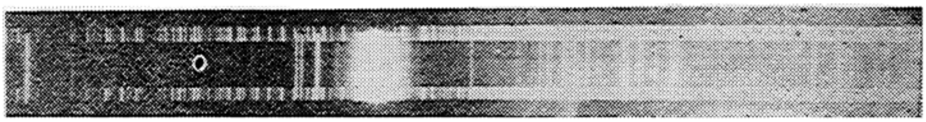
$\alpha$-Furfuryl alcohol $C_4H_3O{\cdot}CH_2{\cdot}OH$



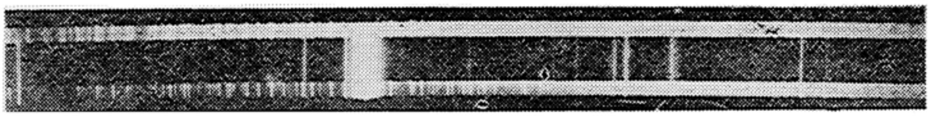
α-Furfuryl acetate $C_4H_3O \cdot CH_2 \cdot O \cdot OC \cdot CH_3$



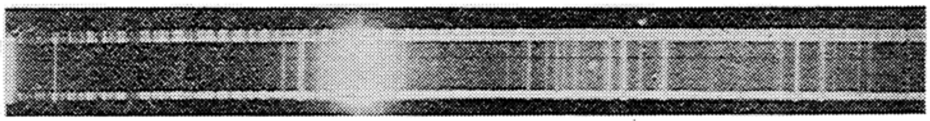
α-Furfural $C_4H_3O \cdot CO \cdot H$



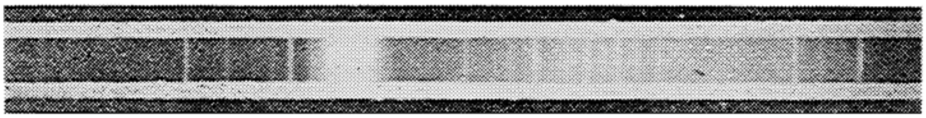
α-Furoyl chloride $C_4H_3O \cdot CO \cdot Cl$



Methyl α-furoate $C_4H_3O \cdot CO \cdot O \cdot CH_3$

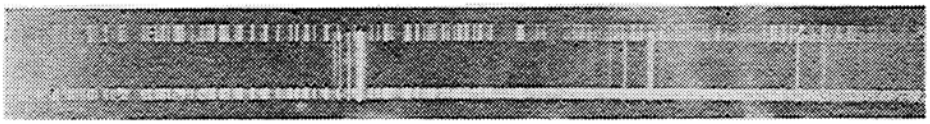


Ethyl α-furoate $C_4H_3O \cdot CO \cdot O \cdot C_2H_5$ (in benzene)

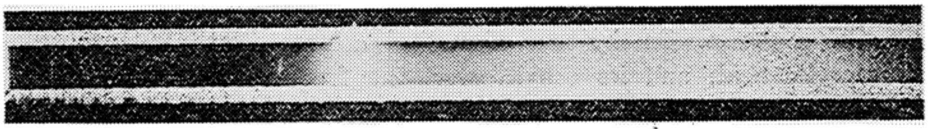


α-Furfuracrylic acid $C_4H_3O \cdot CH : CH \cdot CO \cdot OH$ (in alcohol)

Ethyl α-furfuracrylate $C_4H_3O \cdot CH : CH \cdot CO \cdot O \cdot C_2H_5$



Tetrahydro-α-furfuryl alcohol $C_4H_7O \cdot CH_2 \cdot OH$



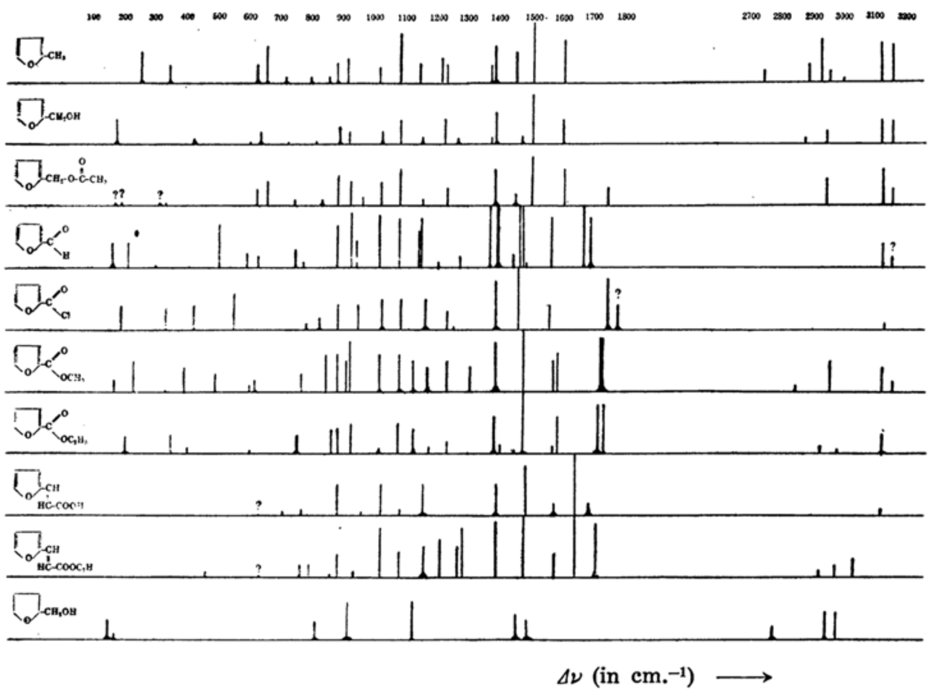
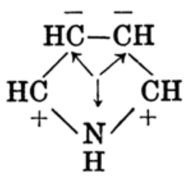



Fig. 1.

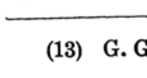


The frequency of 1530 cm.$^{-1}$ is only observed in the case of $\alpha$-derivatives of pyrrole. In the case of $\alpha$-derivatives of furan, however, the intense lines corresponding to the frequency of 1460 and 1507 cm.$^{-1}$ are observed. The frequency of $\Delta\nu$, 1460 cm.$^{-1}$, is found also in furfural and furoyl chloride which do not possess $-CH_2-$ group in their molecules. The frequency of $\Delta\nu$, 1450 cm.$^{-1}$, is generally considered as due to the transversal vibration of the $-CH_2-$ group. In the case of methyl $\alpha$-furoate, ethyl $\alpha$-furoate, $\alpha$-furfuracrylic acid, and its ethyl ester, the frequency of 1478 cm.$^{-1}$ is observed. The frequency of 1460 cm.$^{-1}$ in furoyl chloride, those of 1463 and 1476 cm.$^{-1}$ in furfural are observed. It is better not to attribute these frequencies in furan derivatives to the transversal vibration of the $CH_2$-group, for $CH_2$-group is not found in $\alpha$-furoyl chloride and furfural molecules. So these frequencies in question and that of 1507 cm.$^{-1}$ in $\alpha$-methyl-furan, $\alpha$-furfuryl alcohol, and $\alpha$-furfuryl acetate are considered as associated with the furan ring. Geo. Glockler and B. Wiener[13] have reported quite recently that the frequencies of 624, 758, 878, 1021, 1078, 1156, 1378, and 1467 cm.$^{-1}$ are due to the furan ring and 1567 cm.$^{-1}$ is attributed to the C=C bond. From the fact that the frequency of 1607 cm.$^{-1}$ is found in $\alpha$-methyl-furan, $\alpha$-furfuryl alcohol, and $\alpha$-furfuryl acetate, the formula with double bonds, instead of the centric formula, is supported by the present investigation, since the frequency of 1607 cm.$^{-1}$ is generally accepted as due to the vibration of $-C:C-$. If we take the frequency of 1572 cm.$^{-1}$ in methyl $\alpha$-furoate, ethyl $\alpha$-furoate, and ethyl $\alpha$-furfuracrylate, and the frequency of 1563 cm.$^{-1}$ in furfural and $\alpha$-furoyl chloride, as corresponding to the frequency of 1607 cm.$^{-1}$ in $\alpha$-methyl-furan, etc., it seems that the formula with double-bonds is more probable than the centric formula for the furan ring, at least, in $\alpha$-derivatives. The further discussion will be reported after studying the Raman spectra of furan itself, its $\beta$ and other derivatives, which are now in the course of experiments.

## Summary.

(1) The Raman spectra of the following substances have been measured: $\alpha$-methyl-furan, $\alpha$-furfuryl alcohol, $\alpha$-furfuryl acetate, furfural, $\alpha$-furoyl chloride, methyl $\alpha$-furoate, ethyl $\alpha$-furoate, $\alpha$-furfuracrylic acid, ethyl $\alpha$-furfuracrylate, and tetrahydro-$\alpha$-furfuryl alcohol.

(2) The frequencies of $\Delta\nu$, 625 (or 650), 888, 925, 1021, 1081, 1153, 1232, 1390, 1460 (or 1480), 1507, 1575 (or 1605), 3122, 3153 cm.$^{-1}$, are observed as the characteristic lines of the $\alpha$-mono-derivatives of furan.

(3) The frequencies of $\Delta\nu$, 1460 (or 1480) and 1572 cm.$^{-1}$, are observed in the type of , while those of 1507 and 1605 cm.$^{-1}$ in the type of .

(13) G. Glockler and B. Wiener, *J. Chem. Phys.*, **2** (1934), 47.

(4) It is shown that the investigation supports the formula with double bonds in the case of $\alpha$-mono-derivatives of furan.

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