

THE NEAR ULTRAVIOLET ABSORPTION SPECTRUM OF 2-FURFURALDEHYDE

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INTRODUCTION

In 1910, the absorption of 2-Furfuraldehyde in the vapour state was studied by Purvis, who measured 31 bands from λ 2726 to λ 2450 and arranged the wavelengths of 25 of these in a short diagonal array.

The spectrum was studied in solution by Getman (1924) and Hartley and Dobbie (1898). More recently Elkan Blout and Melvin Fields (1948) investigated the spectrum of 2-Furfuraldehyde in Dioxane and reported two absorption maxima, one at 217 $m\mu$ and the other at 310 $m\mu$. It was also examined in alkaline and acid media by Dobrinskaya and Neimann, Polkanova and Protensko (1948) who prepared alcoholic solutions and obtained a single absorption band at 2700 A. A second absorption band was also obtained in alkaline condition at 3400 A, which was absent in acid or neutral alcoholic solution. In 1950 Raffau reported two absorption maxima at 230 and 275 $m\mu$ in solution.

The most important work on the absorption of the molecule in the vapour state is that of Walsh (1946) who studied the absorption with a vacuum spectrograph in the region below 2700 A. He reported three regions of absorption, one at 2600 A (for which a spectrogram taken on a vacuum spectrograph was reproduced under small dispersion), the second with maximum lying at 1800 A (in this, the frequencies of seven diffuse bands were reported, involving two prominent wave number intervals, 887 cm.^{-1} and 230 cm.^{-1}) and the third consisting of diffuse bands from 1600 A onwards. Discussing the character of the spectrum, the bands in the 1600 A region are interpreted as analogous to those of Furan occurring in the same region. These are ascribed to be of the Rydberg type, the π ionisation potential of 2-Furfuraldehyde having nearly the same value as that of Furan. The bands at λ 2600 were tentatively assigned to the $N-V_1$ transition of the π electrons of 2-Furfuraldehyde. Further assignments were stated by him to be too speculative, but mentioned that one would expect a transition of the type $N \rightarrow A$ to occur between λ 3000 and λ 4000, though no such absorption was reported.

While examining the absorption spectra of Furan and a number of other available substituted Furans, it has been noticed that 2-Furfuraldehyde exhibited in the vapour condition a very rich and extensive absorption spectrum (λ 2800– λ 2450) with many more bands than were recorded by Purvis. The complete analysis and interpretation of the system are reported in this paper.

The Raman spectrum of the molecule was photographed by Bonino and Manzoni-Ansidei (1934) who established 13 Raman lines. Glockler and Wiener (1934) have also studied the Raman effect of 2-Furfuraldehyde using λ 4358 Hg line excitation and NaNO_2 filter. 17 lines were reported, 8 being assigned to the skeletal vibrations, 5 to the α -substituted CHO and the remaining 4 to C=C, C=O, C-H (Aliphatic) and C-H (Aromatic) vibrations as indicated in Table 1.

TABLE I

Furan	2-Furfur- aldehyde			
604	624		172	
735	758	} due to the skeleton	497	
857	878		581	
990	1021		929	
1055	1078		1221	
1139	1156		1567	
1381	1378		1677	
1486	1467		2881	
			3129 (aromatic) C—H	
				} due to α -substituted CHO group.
				C = C
			C = O	
			C—H in (HC = O group)	

In 1949 Rolla and Chiorboli investigated the Raman spectrum in solutions of different concentrations. All the Raman lines together with the visual estimates of the intensities of the lines used in this work are those given by Magat (1936).

No data, however, concerning the depolarisation factors for the Raman lines are available, nor has the infra-red spectrum of the molecule been recorded satisfactorily. A qualitative study of the polarisation characteristics of the Raman lines has been carried out in this work in order to facilitate the interpretation of the spectrum.

RESULTS

The specimen 2-Furfuraldehyde used in this investigation was supplied by the Light Chemicals and Co.; it is a liquid having boiling point 161.7°C. under atmospheric pressure. The specimen is redistilled under reduced pressure and the distillate is collected directly into the container of the absorption tube. Different absorbing columns have been used varying from 5 to 100 cm. the liquid container being kept at temperatures from -15° to 65°C .

The band system extends from λ 2700 down to λ 2450. Not much difference was found between the spectra taken at 0°C . and at -15°C . The system consists of several distinct groups with marked regularities. Six of such groups (*A* to *F*) could be seen in Plate VI (*a*). The strongest components of these six groups are at 37107, 37309, 37487, 37668, 37849, and 37990 cm^{-1} which give the impression of nearly equispaced bands but the intervals vary widely. Further towards the violet, the resolution of the components in each group is not so clearly evident, but about 14 unresolved and somewhat diffuse bands could be measured. These are shown in Plate VI (*b*). When the temperature of the container is at 28°C . there is total absorption below λ 2580 with a very few bands towards the red end of ν 37107. The intensity and the spread of the band at ν 37107 are so much enhanced that the band is almost merged into the total absorption region. At this temperature and at higher temperatures, the region of the spectrum above λ 2700 is developed gradually with the increasing temperatures.

Plate VII (*a*, *b*, *c*) reproduced the medium quartz spectrogram with 50 cm. vapour column when the temperature of the container is varied from -15°C . to 28°C . The development of the spectrum in the region of longer wavelengths is prominently observed. A few additional bands are recorded on the long wavelength side of ν 37107 when the vapour column is 100 cm. long and the container is kept at 0°C . and 28°C . At 65°C . total absorption is obtained commencing from λ 3000 and extending down towards the violet.

Measurements have been made on different Littrow and Medium Quartz plates for recording the spectrum in the entire region from the violet towards the red. Altogether 163 band heads have been measured. Their wavelengths, intensities and wave numbers are collected in Table 3. The intensities are visual estimates, as these are from different plates for different regions. The following intensity classification is adopted. The symbols 'es' denote extremely strong, 'vs'—very

strong, 'st'—strong, 'bd'—broad and diffuse, etc. The wavelengths are given to the first decimal place only since the bands generally are diffuse and the wave numbers to the nearest integer.

There is a second region of absorption—a very weak one from $\lambda\lambda$ 3700–3300 with a strong band at λ 3521.9 (ν 38286). This was photographed when the vapour column was 50 cm. long and the liquid at 28°C. Eleven diffuse band heads could be observed in this second region and measured approximately. The individual bands show no group structure such as is found in the first system. The wavelengths of the bands of this system are given in Table 4.

Analysis and Discussion ($\lambda\lambda$ 2800–2450)

Group theoretical methods have recently been used successfully in a number of investigations for analysing and interpreting the structure of the complicated spectra of benzene and its derivatives in the near ultraviolet region. While the high symmetry of benzene imposes a number of limitations on the interpretation of its spectrum, no such restrictions exist as stated by Sponer, for a five ring molecule like Furan, C_4H_4O . Furan has a symmetry C_{2v} with eight totally symmetrical vibrations, the other vibrations being three of A_2 , seven of B_1 and three of B_2 type. The identification and the assignment of the Furan vibrations have been discussed by Reitz (1938), Pickett (1942) and Thompson and Temple (1945) from measurements on the Raman, infra-red and ultraviolet absorption spectra.

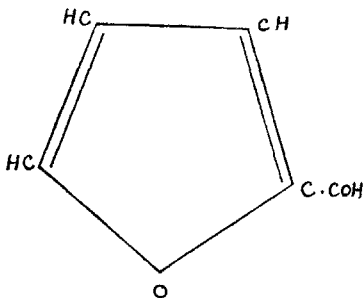


FIG. 1

In 2-Furfuraldehyde (Fig. 1), the symmetry of Furan is lowered to C_s by a mono-substitution of COH in the 2-position, assuming the molecule to be planar. This provides only two electronic and two vibrational levels that are symmetric and anti-symmetric to the molecular plane. The division of the 21 vibrations of the molecule into these two types, the selection rules and the classification as to the nature of the vibrations are given in Table 2 in comparison with those of the parent molecule, Furan. The electronic transition probabilities are determined by the matrix

elements of the di-pole moment $\int \psi_{ei}^* M \psi_{ei}$ where ψ_{ei}' and ψ_{ei}'' are the electronic

eigen-functions in the upper and lower states, ψ^* indicates the complex conjugate value and M is the di-pole moment of the system of nuclei and electrons in different electronic configurations. In a C_s point group, all the transitions are allowed. With fifteen totally symmetric vibrations, the possibilities of interpreting the bands will be many and a large number of bands may be caused by the superposition of several different vibrations.

The observed spectrum consists of several distinct groups with a pronounced regularity in the components both in magnitude and in intensity. In carrying out the analysis, the pure electronic transition, i.e. 0, 0 band, expected in the first group on the long wavelength side is identified at first at 37107 cm.^{-1} , which is

TABLE 2

		FURAN						2-FURFURALDEHYDE					
C_{2v}	E	C_2	σ_h	σ_v	No.	Classification	R	I.R.	C_s	No.	R	I.R.	Classification
A_1	1	1	1	1	8	$\left\{ \begin{array}{l} 4 \text{ Ring stretching} \\ 2 \text{ C-H stretching} \\ 2 \text{ C-H bending} \end{array} \right\}$	a	a					$\left\{ \begin{array}{l} 7 \text{ Ring stretching} \\ 3 \text{ C-H} \\ 1 \text{ C-COH valence} \\ 3 \text{ C-H bending} \\ 1 \text{ C-COH bending} \end{array} \right\}$
A_2	1	1	-1	-1	3	$\left\{ \begin{array}{l} 1 \text{ Ring} \\ 2 \text{ C-H} \end{array} \right\}$ deformation	a	ia	-A	16	a	a	a
B_1	1	-1	1	-1	7	$\left\{ \begin{array}{l} 3 \text{ Ring} \\ 2 \text{ C-H} \\ 2 \text{ C-H} \end{array} \right\}$ stretching bending	a	a		6	a	a	$\left\{ \begin{array}{l} 2 \text{ Ring} \\ 3 \text{ C-H} \end{array} \right\}$ deformation $\left\{ \begin{array}{l} 1 \text{ C-COH} \\ \text{deformation} \end{array} \right\}$
B_2	1	-1	-1	1	3	$\left\{ \begin{array}{l} 1 \text{ Ring} \\ 2 \text{ C-H} \end{array} \right\}$ deformation	a	a					

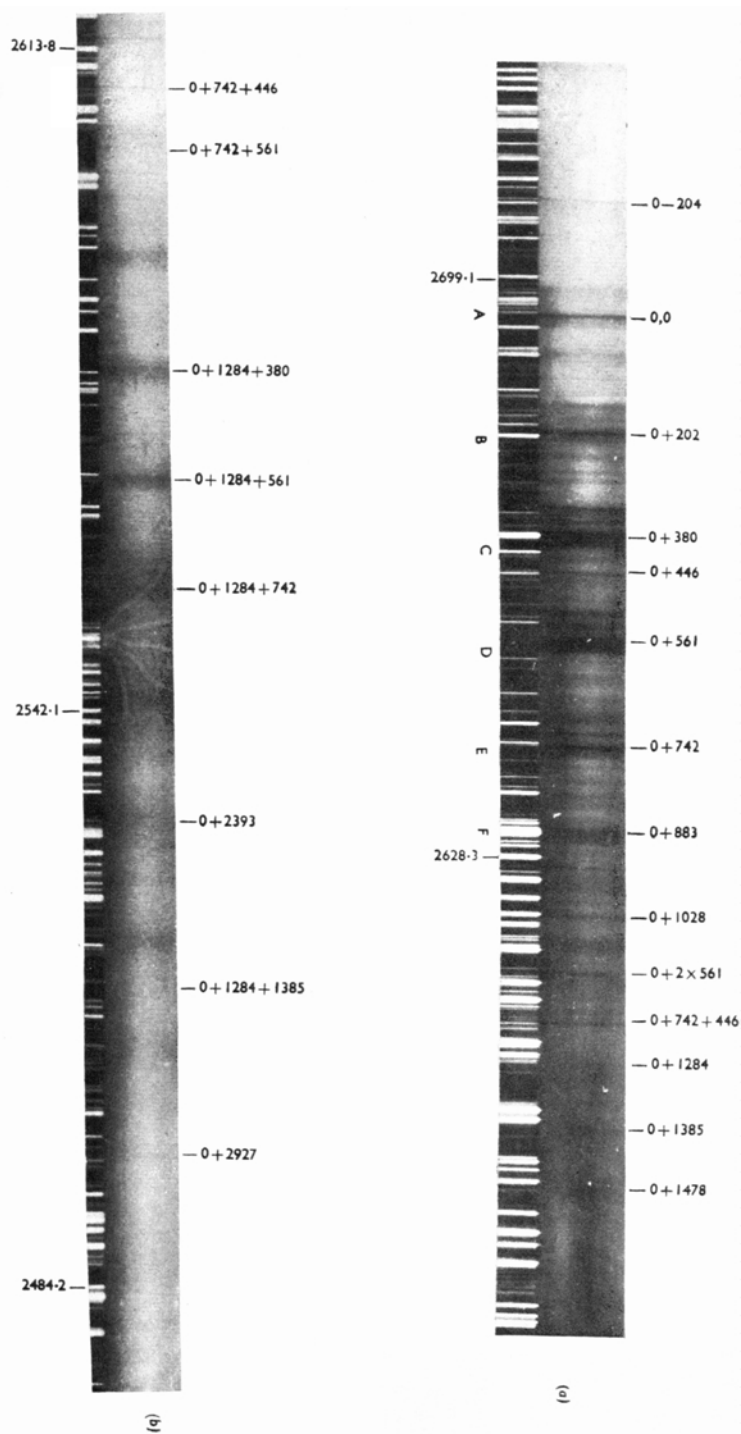
the strongest band in group A. Towards the red side of this band about 40 heads have been measured. These appear under different conditions as they correspond to different Boltzmann factors. A number of ground state frequencies have been identified in this region with the help of the Raman data of the spectrum (Table 3). These are 204, 290, 616, 742, 878, 1149 and 1359, agreeing with the Raman frequencies recorded by previous investigators (Table 3) and confirming the location of the 0, 0 band.

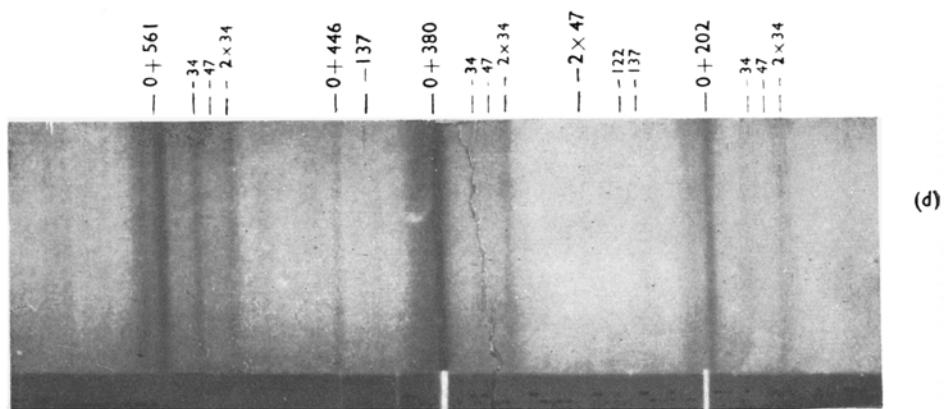
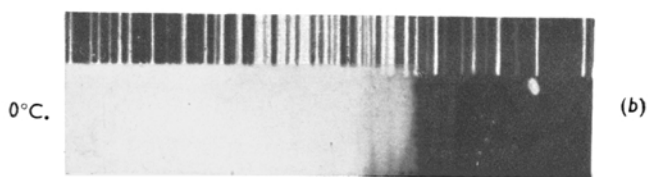
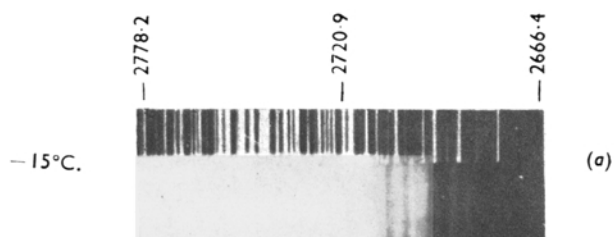
TABLE 3

Ground state			Excited state	
Raman	Int.	U.V. absorption	U.V. absorption	Assignment
172	.			
218	2	204		
296	1	290	202	
500	3		380	C-COH deformation
587	2			
630	2	616	446	Ring
755	2	742	561	Ring
771	1			
879	3	878	742	Ring
927	4			
947	3			
1020	3			
1078	3			
1155	5	1149	1028	Ring
1219	3		883*	C-COH valence
1365	5	1359	1284	Ring
1466	5		1385	Ring
1476	5			
1566.5	3		1478	Ring
1677	6			
2813	2			
2870	2			
3100	1		2393	
3126	3		2927	
3147	4			

*For the correlation of this frequency refer to page 265.

The characteristic excited state frequencies of the molecule should give rise to bands towards the violet end of the 0, 0 transition ν 37107. This region as mentioned earlier represents a rich succession of band groups. The most intense bands of the several groups could be expressed as combinations of the type $0 + m\nu_i + N\nu_j$ and overtones such as $0 + m\nu_i$ or $0 + n\nu_j$, etc., where ν_i , ν_j correspond to the excited state frequencies of the molecule, m and n taking values 1, 2, 3, All the groups could be analysed involving mainly the following frequencies 202, 380, 446, 561, 742, 883, 1028, 1284, 1385, 1478, 2393 and 2927. Several bands have to be interpreted as superposition of two or more transitions. This is a feature usually found while dealing with combinations between several totally symmetrical vibrations. It is found also in the analysis of other similar band systems. Very long progressions of the kind $0 + m\nu$, m ranging up to high values as are commonly observed in symmetrical molecules such as para substituted benzenes, are absent in this spectrum. This may be expected in a C_s symmetry. There are two other frequencies 825, 1124 whose identification as fundamentals cannot be definite. These may be combinations, $446 + 380$, $380 + 742$ respectively. Similarly the





frequency 1478 may be regarded as a combination of 446 and 1028 but, as pointed out later, it is to be interpreted as a fundamental ring frequency, this interpretation being consistent with the intensity of the band. Possible correlation between the ground and the excited state frequencies may be suggested, in which the values in the excited electronic state are taken as somewhat lower than those of the same vibrations in the ground state—an observation drawn from a study of the spectra of molecules of this type so far investigated, e.g. Benzene, Toluene and their substitutions, Pyridine, etc. Such a correlation is shown in Table 3.

The pattern of an individual group may now be referred to. It is best studied by examining and comparing the structure of 2 or 3 groups which are prominent. These are reproduced on an enlarged scale in Plate VII (*d*). The small frequency separations such as 22, 34, 47, etc., towards the red of the 0, 0 band may be taken to represent differences between the vibrations in the ground and the upper electronic states. Transitions such as 1-1, 2-2, v-v of these vibrations can be inferred to be stronger than 1-0 or 0-1 transitions of the same vibrations. The interval 22 may be 587~561, 47 may be 927~883, 95 may be 2×47 , 122 may be 1149~1028, or 500~380, 137 may be 878~742 or 587~446, 190 may be 927~742. Besides this correlation there may be other possibilities by taking two-fold excitation of certain vibrations and forming combinations.

Table 4 gives the analysis that is obtained of the entire band system; the last column gives the interpretation in terms of the identified frequencies. It is difficult to determine uniquely the interpretation of any particular band. The general structure however may be relied on and the ground and excited state frequencies may be taken as real and substantially established. In Table 3 the characteristic frequencies are collected, the probable correlation between the ground and the excited state values is also shown.

TABLE 4

Wavelength in A.U. (λ)	Int.	Wave number in cm.^{-1} (ν)	$\Delta\nu$ from 0, 0	Assignment
2796.5	?	35748	1359	0-1359
2784.2	?	35906	1201	0-1149-47
2780.2	ms	35958	1149	0-1149
2775.1	vw	36024	1083	0-1359-290+561
2769.4	?	36098	1009	0-878-137
2767.6	vb	36122	985	0-1359+380
2764.5	st	36162	945	0-1149+202
2763.5	w	36175	932	0-878-22-34
2761.4	bd	36203	904	0-878-22
2759.4	vb	36229	878	0-878
2757.8	ms	36250	857	0-742-47-2×34
2755.3	b	36283	824	0-742-47-34
2754.0	ms	36300	807	0-742-47-22
2752.7	st	36317	790	0-742-47
2750.8	d	36342	765	0-1149+380, 0-742-22
2749.1	vb	36365	742	0-742
2748.0	bd	36379	728	0-616-47-2×34
2745.6	d	36411	696	0-616-47-34
2744.0	b	36432	675	0-878+202
2743.0	w	36446	661	0-616-47
2741.9	st	36460	647	0-616-34
2739.6	st	36491	616	0-616
2737.2		36523	584	0-1149+561
2735.7	st	36543	564	0-290-2×137
2726.4	w	36668	439	0-2×204-34

TABLE 4—*contd.*

Wavelength in A.U. (λ)	Int.	Wave number in cm. $^{-1}$ (ν)	$\Delta\nu$ from 0, 0	Assignment
2724.4	w	36695	412	0-290-22, 0-2 \times 204, 0-616+202
2715.3	vw	36817	290	0-290
2714.3	vw	36831	276	0-204-2 \times 34, 0-2 \times 137
2712.5	vw	36855	252	0-204-47
2710.7	?	36880	227	0-204-22
2709.0	st	36903	204	0-204
2708.0	bd	36917	190	0-190
2705.9	?	36945	162	0-162
2704.1	ms	36970	137	0-137
2703.0	bd	36985	122	0-122
2701.0	w	37012	95	0-95, 0-2 \times 47
2700.2	?	37023	84	A 0-34-47
2699.2	vs	37037	70	0-2 \times 34
2697.5	st	37060	47	0-47
2696.6	bd	37037	34	0-34
2695.7	ms	37085	22	0-22
2694.1	vs	37107	0	0-0
2693.3	vb	37118	-11	0+202-190
2690.8	vw	37153	-46	0+202-162, 0-202-137-22
2689.3	st	37173	-66	0+202-137
2688.4	bd	37186	-79	0+202-122
2687.2	vw	37202	-95	0+380-290
2686.3	ms	37215	-108	0+202-2 \times 47
2684.9	w	37234	-127	0+202-47-34
2682.9	st	37262	-155	0+202-47, 0+742-584
2681.9	bd	37276	-169	0+202-34
2681.1	ms	37287	-180	0+202-22, 0+380-204
2680.1	?	37301	-194	0+380-190
2679.5	vs	37309	-202	0+202
2678.5	vb	37323	-216	0+380-162
2676.5	b	37351	-244	0+380-137
2675.6	vw	37364	-257	0+380-122
2674.6	ms	37378	-271	0+561-290
2673.5	ms	37393	-286	0+380-2 \times 47
2672.3	vw	37410	-303	C 0+380-47-34
2674.2	vw	37425	-318	0+380-2 \times 34
2670.0	vs	37442	-334	0+380-47
2669.2	st	37453	-346	0+380-34
2668.5	ms	37463	-356	0+380-22, 0+561-204
2667.7	w	37474	-367	0+561-190
2666.8	es	37487	-380	0+380
2665.8	vb	37501	-394	0+2 \times 202
2663.8	b	37529	-422	0+561-137
2662.9	?	37542	-435	0+561-122
2662.1	st	37553	-446	0+446
2661.0	bd	37569	-462	D 0+561-2 \times 47
2659.7	vw	37587	-480	0+561-34-47
2658.7	ms	37601	-494	0+561-2 \times 34
2657.2	st	37622	-515	0+561-47
2655.7	st	37644	-537	0+561-22, 0+742-204
2654.8	?	37656	-549	0+742-190
2654.0	vs	37668	-561	0+561
2653.1	vb	37681	-574	0+742-137-34
2651.5	w	37703	-596	0+742-137-34-22
2650.7	d	37715	-608	E 0+742-137, 0+3 \times 202
2649.7	ms	37729	-622	0+742-122
2649.0	ms	37739	-632	0+742-137-22
2648.2	?	37750	-643	0+742-2 \times 47, 0+202+446
2646.9	bd	37769	-662	0+742-47-34

TABLE 4—*contd.*

Wavelength in A.U. (λ)	Int.	Wave number in cm.^{-1} (ν)	$\Delta\nu$ from 0, 0	Assignment
2645.8	vw	37785	678	0+ 742-2×34, 0+ 883-204
2645.1	w	37795	688	0+ 742-34-22
2644.3	st	37806	699	0+ 742-47, 0+ 883-190
2643.4	?	37819	712	0+ 742-34
2642.7	st	37829	722	0+ 742-22
2641.3	vs	37849	742	0+ 742
2640.4	vb	37862	755	0+ 2×380
2638.9	w	37883	-776	0+ 883-34-47-22
2637.9	vw	37898	-791	0+ 883-2×47
2637.1	ms	37909	-802	0+ 883-34-47
2636.2	w	37922	-815	0+ 883-2×34
2635.5	ms	37932	-825	0+ 446+ 380, 0+ 883-22-34, 0+ 1028-204
2634.5	vw	37947	-840	0+ 883-47
2632.6	vw	37974	867	0+ 380+ 561-47-34
2631.5	vs	37990	883	0+ 883
2630.5	vb	38004	897	0+ 2×446, 0+ 1028-137
2628.6	st	38032	925	0+ 2×561-204
2627.1	st	38053	946	0+ 380+ 561, 0+ 742+ 202
2626.2	vw	38066	959	0+ 2×561-162
2625.4	vw	38078	971	0+ 1028-22-34
2624.6	vs	38090	983	0+ 1028-47, 0+ 2×561-137
2623.9	?	38100	993	0+ 1028-34
2623.1	ms	38111	1004	0+ 1028-22, 0+ 446+ 561, 0+ 2×561-122
2621.5	vs	38135	1020	0+ 1028, 0+ 2×561-2×47
2620.6	?	38148	1041	0+ 561-34-47
2618.5	vb	38178	1071	0+ 2×561-47
2616.3	?	38211	1104	0+ 2×561-22
2614.9	st	38231	1124	0+ 2×561, 0+ 1284-162
2613.8	?	38247	1140	0+ 3×380
2613.1	vw	38257	1150	0+ 1284-137
2612.2	b	38270	1163	0+ 1284-122
2610.6	ms	38294	1187	0+ 742+ 446, 0+ 1284-2×47, 0+ 1478-290
2609.4	b	38312	1205	0+ 1284-34-47, 0+ 2×380+ 446
2607.5	?	38339	1232	0+ 1284-22-34, 0+ 1028+ 202
2604.0	vb	38391	1284	0+ 1284, 0+ 1478-190
2602.6	b	38412	1305	0+ 1478-162, 0+ 742+ 561
2600.3	bd	38446	1339	0+ 3×446, 0+ 1478-137
2598.7	w	38469	1362	0+ 1478-122
2597.2	bd	38492	1385	0+ 1385, 0+ 1478-2×47
2596.4	?	38503	1396	0+ 1478-47-22
2594.8	?	38527	1420	0+ 1478-2×34
2590.9	st	38585	1478	0+ 1478, 0+ 1028+ 446
2590.2	vw	38596	1489	0+ 2×742, 0+ 1284+ 202
2589.4	ms	38607	1500	0+ 380+ 2×561, 0+ 742+ 2×380
2586.6	bd	38649	1542	0+ 1478+ 202-137
2581.0	?	38733	1626	
2579.1	w	38762	1655	
2578.3	ms	38774	1667	0+ 1284+ 380
2577.6	?	38784	1677	0+ 1478+ 202
2569.7	vw	38903	1796	0+ 1028+ 2×380
2568.1	vw	38928	1821	
2566.5	st	38952	1845	0+ 1284+ 561
2565.1	?	38972	1866	0+ 2×561+ 742, 0+ 1478+ 380
2561.8	vw	39023	1916	0+ 1028+ 883
2557.0	?	39097	1990	
2554.7	vb	39132	2025	0+ 1284+ 742

TABLE 4—concl'd.

Wavelength in A.U. (λ)	Int.	Wave number in cm. ⁻¹ (ν)	$\Delta \nu$ from 0, 0	Assignment
2550.3	w	39199	2092	0 + 4 × 202 + 1284
2545.7	vw	39270	2163	0 + 1284 + 883
2543.5	vb	39304	2197	0 + 2393 - 204
2540.1	vw	39357	2250	0 + 2393 - 137
2537.5	ms	39397	2290	
2530.9	bd	39500	2393	0 + 2393, 0 + 1385 + 561 + 446
2528.4	vw	39539	2432	
2525.3	bd	39587	2480	
2520.4	vw	39660	2553	0 + 2 × 1284 ?
2518.9	vb	39688	2581	0 + 2393 + 202
2513.7	vb	39770	2663	0 + 1284 + 1385
2509.1	?	39843	2736	0 + 2927 - 190
2507.5	vw	39870	2763	0 + 1478 + 1284, 0 + 2 × 1385
2502.3	vw	39951	2844	0 + 2393 + 446
2500.1	vw	39986	2879	0 + 2927 - 47
2497.0	bd	40034	2927	0 + 2927
2491.9	vw	40118	3011	0 + 2927 + 380 - 290
2485.4	w	40304	3197	0 + 2393 + 883 - 34 - 47
2474.8	vb	40395	3288	0 + 2393 + 883
2469.6	vw	40480	3373	0 + 2927 + 446
2464.0	vb	40574	3467	0 + 2927 + 742 - 204
2458.8	vw	40658	3551	

II SYSTEM

Wavelength in A.U.	Int.	Wave number in cm. ⁻¹
3693	vw	27071
3679	vb	27074
3659	?	27332
3543	st	28217
3535	vw	28280
3522	st	28385
3503	ms	29539
3492	vw	28029
3455	ms	28935
3401	vb	29395
3306	b	30212

ASSIGNMENT OF VIBRATIONS

The definite assignment of vibrations is difficult in the absence of observations in the infra-red and quantitative determinations of depolarisation factors of Raman lines. However a comparison may be made with certain vibrations which are well established in Furan. For the ground state of Furan, Thompson and Temple (1945) have established 4 totally symmetric ring vibrations, 724, 994, 1381, 1486, of A_1 type and one, 1579, of B_1 type from the studies in the infra-red. For 2-Furfuraldehyde of C_s symmetry both A_1 and B_1 types of Furan vibrations will give rise to the A' type (see Table 2). One would therefore expect in this case not only the four A_1

totally symmetrical ring vibrations but also the three ring vibrations of B_1 type, i.e. 7 totally symmetrical ring vibrations.

In 2-Furfuraldehyde, the ground state frequencies 755, 879, 1365, 1476 and 1566.5 may be the five corresponding ring vibrations. The qualitative observations of the polarisation characteristics of these lines indicate the totally symmetrical character of these vibrations. The first three of these, 755, 879, 1365 (742, 878, 1359 as measured on spectrograms, on quartz spectrographs), are also found in the ultraviolet absorption, the remaining two 1476 and 1566.5 have not appeared probably due to large Boltzmann factors. The assignment is further confirmed by the detection of the correlated vibrations in the excited state, namely 561, 742 1284, 1385 and 1478, which give rise to intense band heads and strong combination bands.

Besides these five, two more ring vibrations are expected in 2-Furfuraldehyde, related to the remaining Furan vibrations of B_1 type. From a consideration of the intensity of the absorption, 616 and 1149 of the ground state may be suggested as the two vibrations of this type. In Furan, the corresponding values are presumed to be 624 and probably 1137*, 624 having been assigned by Pickett as a Furan ring vibration of B_1 type. This interpretation of the seven ring vibrations is substantially consistent with the suggestion made by Glockler and Wiener from Raman effect observations. Reference may be made to Table 1 given earlier.

Besides the ring vibrations, four of the totally symmetric deformation vibrations may be expected—3 of C-H and one of C-COH (ref. Table 2).

The C-H deformation vibrations in Furfuraldehyde presumably are of the same order of magnitude as in Furan. Comparison would at first suggest 1020 and 1078 as two of these frequencies. This however cannot be taken as definite as Glockler regarded these as skeletal vibrations. It may also be stated that in the ultraviolet, corresponding excited state frequencies could not be detected (see Table 3). If they are skeletal vibrations they should be of non-totally symmetric character. †Further investigation is needed to clarify the nature of these frequencies and the definite identification of C-H vibrations.

Five other frequencies‡ 172, 497, 581, 929 and 1221 were assigned as due to the α substituted COH group. In the present investigation these frequencies are not detected in the ground state in combinations towards the red of the 0, 0 band. However 380 and 883 of the excited state give rise to combinations with other identified ring frequencies. Perhaps 380 could be associated with the value 497 of the ground state which may represent the C-COH inplane deformation, the other frequency 883 may be the C-COH valence vibration; if so, it should more probably be correlated with the ground state frequency 1221 which is of the right order of the magnitude for C-COH valence vibration.

The vibrations of C-H stretching type may now be considered. These are usually of the order of 3000 cm^{-1} . Glockler has suggested 2881 and 3129 as C-H aliphatic and C-H aromatic frequencies. In the ground state these two frequencies give bands too far towards the red of the 0, 0 transition, to be observed in the ultraviolet absorption. Two frequencies 2393 and 2927 in the excited state are found to give combinations towards the violet of the 0, 0 band. If these prove genuine, these may be regarded as corresponding to C-H stretching in the excited state, both of them being totally symmetric.

* This is ascribed to be A_1 type ring vibration by Reitz, and as a C-H deformation of A_1 type by Thompson and Temple. But whatever the assignment might be, it is definitely a totally symmetrical vibration. Pickett (1940) suggested from the far ultraviolet data that it is a ring vibration.

† Observations on the polarisation characteristics with respect to these frequencies are not very conclusive.

‡ Glockler's values are quoted here.

SUMMARY

The absorption of 2-Furfuraldehyde in the vapour state has been investigated in the region λ 3700– λ 2450. An intense and extensive system consisting of groups (with 163 bands in all) in the region λ 2800– λ 2450 and another diffuse system consisting of only eleven bands in the region λ 3800– λ 3300 have been obtained. An analysis of the first system is given in terms of the upper state frequencies 202, 380, 446, 561, 742, 883, 1028, 1284, 1385, 1478, 2393 and 2927, the 0, 0 band being located at ν 37107. The assignment of the frequencies has been discussed by comparison with Furan ring vibrations. It has been concluded that 446, 561, 742, 1028, 1284, 1385 and 1478 represent the totally symmetric ring vibrations. The interpretation is consistent with the qualitative observations of the polarisation characteristics of the Raman lines. The second system could not be analysed.

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