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Infrared Absorption Spectra of α and β Monodeutero, and α,α' Dideutero Furan Vapours. Heat Capacity and Entropy of Furan

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The infrared absorption spectra of gaseous α and β monodeutero, and α,α'dideutero furan have been recorded in the 400—3 300 cm^{-1} region on a Beckmann I.R.3 instrument using KBr, NaCl, and LiF optics. Values for the fundamental vibrational frequencies were found or proposed in all three cases. A list of the normal vibration frequencies of furan is presented. Values of the heat capacity and the entropy are discussed.

In connection with microwave work on the deuterated furans [1] infrared absorption curves of three isotopic species were taken primarily as a check of their purity. A study of the literature on the infrared absorption of ordinary furan [2] revealed, however, that a complete vibrational assignment has not yet been given for this molecule. Therefore, a more thorough study of the spectra of the deuterated derivatives was undertaken in the hope that the problem of finding the normal vibration frequencies of furan might be solved or considerably clarified. Since only comparatively small samples were at disposal (0.5—1.5 g) which furthermore had to be conserved for conversion to deuterated pyrroles we had to omit to take infrared and Raman spectra of *liquid* samples. This disadvantage is to a large extent compensated for by the fact that for furan proper both infrared (*e. g.* this investigation) and Raman spectra [3] of the liquid have been reported.

EXPERIMENTAL

A detailed description of the preparations has been given elsewhere [1]. Infrared spectra of the vapours at 30° C and p = 50 and 350 mm Hg in each case were measured in an absorption cell 10 cm in length. The spectroscope was a Beckmann I.R.3 instrument (effective slit-width 2—5 cm^{-1}). In Table 1 observed peak frequencies and important minimum points with their corresponding optical densities are given for furan (reinvestigated here) and three deuterated species. The frequencies are thought to be good to ± 1 cm^{-1} absolutely, somewhat better "internally".

Table 1. Observed spectra of gaseous furan, α and β deutero furan, and α,α'dideutero furan in the 400—1 800 cm^{-1} region. Frequencies (F) in cm^{-1}. D = optical density at about 50 mm pressure in a 10 cm gas-cell at 30° C. Lines, thought to originate from isotopic impurities, have been omitted.

Furan		α,α'deutero furan		α deutero furan		β deutero furan	
F	*D*	*F*	*D*	*F*	*D*	*F*	*D*
585 **	0.27	490	0.42	498	0.26	501	0.17
601	0.64	505	0.85	515	0.56		
621	0.41	524	0.62	531	0.38	531	0.18
						547	0.42
725	1.0	550	0.09	585	0.11	568	0.22
744	1.5			600	0.37		
765	1.3	569	0.03	618	0.17	586	0.27
		581	0.03			601	0.60
838	0.03	586	0.03	657	0.08	620	0.45
862	0.45	630	0.07	678	0.07	630	0.43
871	0.54					646	0.48
874 *	0.38	646	0.13	699	0.11	658	0.23
881	0.55						
		667	0.29	721	0.70	667	0.35
984	1.1			738	1.3		
995	0.90	658	0.22	756	1.05	698	0.28
1 005	1.2	678	0.50				
		698	0.28	798	0.66	715	0.35
1 057	0.33			805	0.52	729	0.85
1 067	0.35	698	0.28	815	0.95	750	0.69
1 079	0.34						
ca. 1 140	0.02	751	0.27	815	0.95	750	0.69
1 168	0.59	779	0.80	858	0.10	780	0.39
1 178	0.60	782 *	0.49	866	0.09	799	0.90
1 181 *	0.49	785	0.72	879	0.10	818	0.54
1 184	0.64						
1 192	0.65	779	0.80	860	0.14	818	0.54
		798	1.5			829	0.43
1 259	0.01	815	0.64	903	0.08	837	0.20
1 268 *	0.01			912	0.07		
1 279	0.01	829	0.38	922	0.05	836	0.20
						849	0.30
1 374	0.11	886	0.10	995	0.80	864	0.36
1 384	0.10	904	0.20	1 002	0.80		
1 396	0.10	919	0.09	1 005 *	0.60	874	0.80
				1 016	0.85	886	0.60
ca. 1 460	0.23	1 005	0.45			897	0.54
		1 016	0.50	1 075	0.30		
1 478	0.58	1 019 *	0.30	1 089	0.30	1 010	0.56
1 490	0.50	1 028	0.45	1 099	0.33	1 021	0.50
1 500	0.46					1 032	0.52

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* Intensity minimum in the top of a "B"-type band.

** Peak frequencies joined by } are thought to belong to one and the same band.

Furan		α,α′deutero furan		α deutero furan		β deutero furan	
F	*D*	*F*	*D*	*F*	*D*	*F*	*D*
		1 074	0.59	1 166	0.48		
1 577	0.39	1 077 *	0.37	1 169 *	0.40	1 050	0.40
1 586 *	0.30	1 088	0.57	1 174	0.52	1 061	0.43
1 591	0.31					1 074	0.45
		ca. 1 162	0.14	1 219	0.23		
ca. 1 700	0.05			1 230 *	0.17	1 121	0.04
		1 202	0.44	1 238	0.22		
1 713	0.09	1 212	0.43			1 160	0.56
1 729 *	0.03	1 224	0.47	1 306	0.04	1 171 *	0.50
1 735	0.07			1 314	0.05	1 180	0.56
		ca. 1 282	0.05	1 317	0.03		
				1 327	0.05	1 213—62	0.03
		1 306	0.09				
		1 317	0.10	1 363	0.06	1 283	0.01
		1 330	0.09	1 372	0.06	1 295	0.01
				1 382	0.07	1 307	0.02
		1 369	0.04				
				1 447	0.51	1 356	0.07
		1 420	0.60	1 460	0.61	1 367	0.07
		1 434 *	0.54	1 466	0.64	1 378	0.06
		1 438	0.80				
				1 542	0.17	1 438	0.17
		1 500	0.05	1 550	0.13	1 444	0.20
				1 562	0.18	1 457	0.25
		1 541	0.04				
		1 550 *	0.03	1 594	0.09	1 471	0.45
		1 561	0.04	1 598	0.08	1 483	0.42
				1 608	0.10	1 496	0.42
		1 587	0.08	1 626	0.04	*ca.* 1 529	0.15
		1 595 *	0.06	1 636	0.04		
		1 603	0.07	1 646	0.03	1 568	0.18
						1 577	0.22
		1 637	0.03	1 664	0.07	1 589	0.25
		1 645	0.03	1 671	0.05		
		1 653	0.03	1 684	0.08	1 637—72	0.01
		1 689	0.09	1 712	0.06	1 687	0.04
		1 698 *	0.08	1 724	0.04	1 696 *	0.03
		1 709	0.11	1 731	0.06	1 709	0.04
		ca. 1 735	0.11				

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* Intensitity minimum in the top of a "B"-type band.

** Peak frequencies joined by } are thought to belong to one and the same band.

DISCUSSION OF SPECTRA

Microwave and electron-scattering experiments[1] have definitely shown that furan is planar with C_{2v}-symmetry. Unlike ten years ago one need no longer discuss the structural problem by means of infrared and Raman data[2], but one may at once state that the normal vibrations of furan are distributed according to their symmetry as summarized in Table 2. This table also surveys the direction of the electrical moment changes. The molecule is thought of as being placed in a Cartesian co-ordinate system which has its origin in the molecular centre of mass. The y-axis is perpendicular to the plane of the molecule. The z-axis lies in the molecular plane and passes through the oxygen atom. The furan selection rules also apply to the α,α'species while the situation for α and β deutero furan has been sketched in Table 3.

It is also convenient to summarize the number of "ring"-, hydrogen bending, and hydrogen stretching frequencies (Table 4, which also gives the planar or non-planar character of the modes).

Table 2. Symmetry properties of normal vibrations and selection rules for furan and α,α'dideutero furan. C_{2v}-symmetry.

Symmetry classes	Response to symm. elements		Electric moment changes parallel to	Non-genuine vibrations T = translation R = rotation	Selection rules for infrared	Number of normal vibrations	
	C_2^z	σ_y				Total	below 1 600 cm^{-1}
A_1	+	+	z	T_z	Active	8	6
B_1	−	+	x	T_x R_y	»	7	5
A_2	+	−	No changes	R_z	Inactive	3	3
B_2	−	−	y	T_y R_x	Active	3	3
			Number of normal vibrations			21	17

Table 3. Symmetry properties of normal vibrations and selection rules for α and β monodeutero furan. C_s-symmetry.

Symmetry classes	Response to symm. elements σ_y	Electric moment changes parallel to	Non-genuine vibrations T = translation R = rotation	Selection rules for infrared	Number of normal vibrations	
					total	below 1 600 cm^{-1}
A′	+	x and z	T_x, T_z, R_y	Active	15	11
A″	−	y	R_x, R_z, T_y	»	6	6
		Number of normal vibrations			21	17

Table 4. Rough geometrical characterization of the normal vibrations. Planar (+); out of plane (−).

		σ_y	Ring vibration	Hydrogen bending vibration	Hydrogen stretching vibration
Furan and α,α'dideutero furan	A_1	+	4	2	2
	B_1	+	3	2	2
	A_2	−	1	2	0
	B_2	−	1	2	0
α and β deutero furan	A′	+	7	4	4
	A″	−	2	4	0

The furan spectrum in the 400—1 600 cm^{-1} region

The Raman spectrum of liquid furan has six polarized lines at 724, 986, 1 061, 1 137, 1 380, and 1 483 cm^{-1}. This strongly suggests that the ***six A_1-class vibrations below 1 600 cm^{-1}*** should be found in the infrared spectrum close to these frequencies, but directly this cannot be verified from the observations. The lines to look for must be of the so-called "A"-type bands (following Badger and Zumwalt's notation [4]), which possess a central peak flanked by two side-bands each with a more or less pronounced maximum. For furan, the asymmetry parameter $\varkappa$ ("S" in the notation of Ref.[4]) is 0.916[1] while ϱ (= $(A—C)/B$, where A, B, and C are rotational constants) is 0.516. Badger and Zumwalt's $x = \pi\,(\nu—\nu_0)\,(2B/kT)^{0.5}$ becomes $(\nu—\nu_0)/16$ cm^{-1} at 30° C where $\nu—\nu_0$ is the frequency difference between a point in the "A"-band (frequency ν) and the band centre ν_0. Extrapolation from the curves in Fig. 2, Ref.[4], gives $\nu \sim 0.70$ for the *maxima* of the side-branches, so that here $\nu—\nu_0 \sim 10$ cm^{-1}. The separation of the "A"-type side branch maxima is therefore about 20 cm^{-1}. — Our recorded infrared absorption curve for gaseous furan has "A"-type bands with centres at 995, 1 067, 1 384, and 1 490 cm^{-1} with corresponding side-band separations 21, 22, 22, and 23 cm^{-1}. No immediate evidence for infrared bands near 724 and 1 137 exists but an infrared band near 724 can easily be hidden by the intense B_2-fundamental which has its band centre at 744. B_2-class vibrations are of the "C"-type bands, easily recognizable by their pronounced Q-branch and the accompanying P and R branches. For such transitions there is approximate validity of the relation [5]

$$\Delta \nu_{P,R} = \frac{S}{\pi}\sqrt{\frac{2\,kT}{I_a + I_b}} \qquad \log_{10} S = \frac{0.721}{\left(\frac{I_a + I_b}{2\,I_c} + 3\right)^{1.13}}$$

(where $\Delta\nu_{P,R}$ is the frequency separation of the P and R branch maxima, $I_a < I_b < I_c$ are the principal moments of inertia) because furan is close to an oblate, symmetric top (I_a close to I_b). Using the correct values of I_a *etc.*[1] one calculates $\Delta\nu_{P,R}$ = 34 cm^{-1}. Fortunately, this prediction may be tested on a B_2-band, which is certainly undisturbed by other bands due to its isolated position, the band with its centre at 601 cm^{-1}. Its $\Delta\nu_{P,R}$ is found to be 36 ± 1 cm^{-1}. Now, for the B_2-band at 744 we find that $\Delta\nu_{P,R} = 40 \pm 1$ cm^{-1}. Since the two $\Delta\nu_{Q,R}$ of the two B_2-bands practically agree it must be the two $\Delta\nu_{P,Q}$'s which differ by about 4 cm^{-1} so that the presence of some disturbance in the P-branch of the 744-band may be postulated. By comparison of the intensity distribution of the two B_2-bands (which should show marked similarities) it is seen that the P-branch of the 744-band is somewhat more intense than expected. *Together*, the arguments presented in favour of speaking of an "observed" line near 724 cm^{-1} (the maximum of the P-branch) seem almost conclusive. It is confirmed by the study of isotopic species.

The other "missing" A_1-fundamental also has an unfavourable anticipated position in the "foot" of the very strong B_1-fundamental at 1 181. This band is of the "B"-type which for furan has less pronounced maxima (if any) in the side-branches so that a check as performed above is impossible. However, an intensity irregularity is clearly visible in the 1 120—1 145 region. Features from the spectra of the deuterated species help to show that there is a fundamental here.

The *five fundamentals of the B_1-class below 1 600 cm^{-1}* are to be "B"-type bands. For furan, these will have a relative intensity *minimum* at the centre flanked by two closely spaced maxima (*separation* 3—5 cm^{-1} which, due to perturbations, may not be observable so that a single *maximum* appears). A "B"-type band terminates in side-bands with or without maxima which, if observable, must be separated about 20 cm^{-1}. Bands with a reasonable resemblance to this description are found at 1 181 (1 171), 1 268 (1 270), and 1 586 (?) (numbers in parentheses are observed, depolarized Raman shifts). A strong, observed band at 874 has some resemblance to, *e. g.*, the A_1-band at 1 067 (although it is far less symmetrical). But since the corresponding Raman line is depolarized and since 874 cannot be a "C"-type band (the bands of the B_2-class) 874 is excluded from other classes than B_1. Data from the isotopic species verify this. — Thompson [2] has questioned whether 1 181 belongs to the B_1-class. In our records of gaseous and liquid furan it is easy to see that the line is disturbed by something in the "foot" (as already mentioned) and something in the "tail", but its central part looks to us as if it were a "B"-type line.

Two out of five B_1-type vibrations at 874, 1 181, 1 268, 1 586, and an unknown frequency are expected to be hydrogen bending vibrations (Table 4). These two can be any of the three at 874, 1 181, and 1 268. Probably we are still lacking one "ring"-vibration. In their paper on pyrrole and deuterated species Lord and Miller [6] found that two "ring"-vibrations in the B_1-class had to be located at 1 418 and 1 530. Obviously, our band at 1 586 corresponds to the pyrrole band at 1 530. Therefore, we may look for another "ring"-vibration in the vicinity of 1 470 cm^{-1}. Actually, a band is observed in the "foot" of the band at 1 490. Its approximate location is 1 455 cm^{-1}. A depolarized Raman line has been observed by Reitz [3] at 1 455. Data from the deuterated species seem to confirm our choice.

Two of *the three B_2-bands* are easily found due to their pronounced "C"-type structure, the bands at 601 and 744 cm^{-1}. As already mentioned by Thompson [2] it might be the intense Q-branch of the third B_2-band that peeps up at 838 in the "foot" of the strong B_1-fundamental at 874. A depolarized Raman line [3] has been observed at 839 cm^{-1}.

The three A_2-fundamentals are not active in the infrared but should appear in the Raman spectrum. An observed Raman line at 1 034 cm^{-1} is naturally assigned to the A_2-class. Confirmation is obtained by considering the infrared spectrum of *liquid* furan. Here, the selection rules may break down and actually a small, but distinct line is observed at 1 030. Roughly speaking, the two remaining frequencies in the A_2-class should lie in the 500—700 cm^{-1} region. An otherwise unexplained line at 1 090 cm^{-1} in the spectrum of liquid furan might be the first overtone of one of the A_2-fundamentals (at *ca.* 545 cm^{-1}). Guthrie *et al.*[7] have suggested that the "B"-type band at 1 268 is the first overtone of one of the A_2-fundamentals, and not a fundamental as suggested by us. Therefore, the third A_2-fundamental could lie at about 640 cm^{-1}. We want to maintain that 1 268 is a fundamental (of the B_1-class) since this gives a natural explanation of the very strong bands at 1 212 and 1 230 in the α and α,α' deuterated species. Of course, this does not exclude that two lines coincide at 1 268 in the spectrum of furan. Indeed, product rule calculations to be given later in this paper indicate that A_2-fundamentals near 1 030, 660, and 550 are highly probable. An observed, weak Raman line at 1 324 cm^{-1} could be the first overtone of a 660-fundamental.

The furan spectrum in the 1 600—3 300 cm^{-1} region

Two overtones of definite "A"- or "B"-type structure are observed at 1 700 and 1 729. Hydrogen stretching frequencies are located at 3 124 and 3 163. Inbetween, quite a few bands (weak) appear but their contours are disappointingly complex and difficult to interpret. We shall, therefore, renounce from an attempt to utilize this part of the absorption curve.

Bands at 1 700 and 1 729 may be interpreted as first overtones or one of the combinations $A_1 + B_1$, $A_1 + A_1$, $B_1 + B_1$, $A_2 + A_2$, $B_2 + B_2$, or $A_2 + B_2$. If there are first overtones at 1 700 and 1 729 there should be fundamentals at 850 and 865. 1 729 may, therefore, be interpreted as $2 \times 874(B_1) = 1\ 748$, being 1 % anharmonic. 1 700 we may explain as $720(A_1) + 995(A_1) = 1\ 715$, also being 1 % anharmonic. These facts leave no room for well-founded speculations as to the magnitude of the missing A_2-frequencies.

The fundamentals finally adopted in this paper for furan are given in Table 7. These values have consequences to be discussed for a comparison between the theoretical and the experimental C_p-curve and the entropy of furan recently studied by Guthrie *et al.*[7].

The α,α'dideutero furan spectrum

This compound has the same symmetry species as furan. Its $\varkappa$ is 0.632 [1]; $\varrho = 0.582$. Badger and Zumwalt's $x = (\nu - \nu_0)/15$ cm^{-1} = 0.75. The "A"-type band side branch separation is, therefore, about 22 cm^{-1}. For "B"-type bands it is the same (if discernable). For "C"-type bands one calculates $\Delta\nu_{P,R} = 33$ cm^{-1}. Since the least moment of inertia here is about the x-axis (in furan it is about the z-axiz) we know that class A_1-vibrations must be of the "B"-type, class B_1-vibrations of the "A"-type, and class B_2-vibrations of the "C"-type while class A_2-vibrations are inactive in the infrared spectrum.

Selection of the fundamentals given in Table 7 is easily carried through under due regard to the intensity, the shape, and the position of the bands except in the case of the A_1-vibration at 698 and the B_1-vibration at 667. The peaks observed at these frequencies lie in the P and R branch of the C-type band at 678. They show up quite distinctly inspite of this but it is impossible to say anything about their band contour. Justification for their choice as fundamentals may, however, be found in the circumstance that the calculated product-rule ratios (Table 5) for the two symmetry classes involved fit tolerably with the anticipated.

Table 5. Calculated and experimental product-rule ratios. $\overset{n}{\Pi}\ (a,K)$ *means the product of the n normal vibration frequencies in the symmetry class K for the a derivative. The corresponding symbol for furan itself is* $\overset{n}{\Pi}\ (o,K)$.

	Product rule ratios		
	Calculated	Observed	Deviation %
$\frac{\overset{8}{\Pi}(o,\ A_1)}{\overset{8}{\Pi}(aa',\ A_1)}$	1.971	2.094	+ 6.2
$\frac{\overset{7}{\Pi}(o,\ B_1)}{\overset{7}{\Pi}(aa',\ B_1)}$	1.888	1.932	+ 2.3
$\frac{\overset{3}{\Pi}(o,\ A_2)}{\overset{3}{\Pi}(aa',\ A_2)}$	1.355		
$\frac{\overset{3}{\Pi}(o,\ B_2)}{\overset{3}{\Pi}(aa',\ B_2)}$	1.364	1.371	+ 0.5
$\frac{\overset{15}{\Pi}(o,\ A_1 + B_1)}{\overset{15}{\Pi}(a,\ A')}$	1.929	2.152	+ 11.6
$\frac{\overset{15}{\Pi}(o,\ A_1 + B_1)}{\overset{15}{\Pi}(\beta,\ A')}$	1.925	2.135	+ 10.9
$\frac{\overset{6}{\Pi}(o,\ A_2 + B_2)}{\overset{6}{\Pi}(a,\ A'')}$	1.345	1.334	− 0.8
$\frac{\overset{6}{\Pi}(o,\ A_2 + B_2)}{\overset{6}{\Pi}(\beta,\ A'')}$	1.345	1.334	− 0.8

An interpretation of combination- and overtones is given in Table 6. Only in one case it is absolutely necessary to assume that an A_2-class vibration is involved, namely the "A"-type band at 1 645. This band might therefore be the first overtone of an A_2-fundamental at about 830. It can also be one of the combinations A_2+B_2 which gives rise to the possibilities 847, 967, and 1 140. Since the two last are too high (compare the spectra of the mono-deuterated derivatives) an A_2-fundamental may lie at 847 cm^{-1}. We shall see later that the existence of an A_2-fundamental near 830-50 agrees well with data from the monodeuterated species.

The α deutero furan spectrum

Here, we have only two symmetry-classes, A′ (planar vibrations, "A"- or "B"-type bands) and A″ (out-of-plane vibrations, "C"-type bands). $\varkappa$ is 0.733. $\varrho = 0.557$ [1]. Again, the "A"- and "B"-type band side branch separation is about 22 cm^{-1} while the $\Delta\nu_{P,R}$ for "C"-type bands is 33 cm^{-1}.

As for the α,α′-derivatives assignment of the majority of the fundamentals is pretty straightforward. In the A′-class 1 598 was preferred to 1 550 in order to obtain good agreement with the product-rule assuming that the band at 699 is a fundamental. 657 was preferred to 678 as a fundamental since it gives the better product-rule fit when the relation $\left[\overset{6}{\Pi}(\alpha,A'')\right]\Big/\left[\overset{6}{\Pi}(\beta,A'')\right] \sim 1.000$ is used (for the β-derivative the six frequencies of the A″-class can be assigned without discussion).

Combination- and overtones are interpreted in Table 6.

The β deutero furan spectrum

The fundamentals adopted and the interpretation of the overtones *etc.* are given in Tables 7 and 6. The line at 698 has not been assigned to the A′-class because of its pronounced "C"-type band structure. We have, therefore, assumed that the missing A′-fundamental is hidden in the strong band at 729.

FINAL ASSIGNMENT OF FURAN FUNDAMENTALS

As a result of the fore-going discussion we are now able to state that probably the fundamentals of furan and the deuterated species here considered are located as given in Table 7.

The two low-frequency A_2-class fundamentals of furan have been estimated to 550 and 660. This is reasonable in view of the position of the corresponding frequencies in the mono-deuterated species. If they were chosen to be higher the product-rule ratios which control their magnitude would deviate unfavourably from the predicted values.

We might finally try to guess the magnitude of the three missing A_2-fundamentals in the α,α′-derivative spectrum. As already mentioned there is some reason to believe that the fundamental of highest frequency is

Table 6. Observed infrared absorption lines explained as combination- and overtones.

	Position	Type	Interpretation
Furan	1 700	A	720(A$_1$) + 995(A$_1$) = 1 715(A$_1$)
	1 729	A	2 × 874(B$_1$) = 1 748(A$_1$)
*a,a′*dideutero furan	550	A	1 212(B$_1$)−667(B$_1$) = 545(A$_1$)
	581	A	1 369(B$_1$)−782(A$_1$) = 587(B$_1$)
	630	C	1 317(A$_1$)−678(B$_2$) = 639(B$_2$)
	646	?	1 434(A$_1$)−782(A$_1$) = 652(A$_1$)
	751	C	1 434(A$_1$)−678(B$_2$) = 756(B$_2$)
	829	?	1 550(B$_1$)−698(A$_1$) = 852(B$_1$)
	904	C	1 434(A$_1$)−505(B$_2$) = 929(B$_2$)
	1 282	A	505(B$_2$)+798(B$_2$) = 1 303(A$_1$)
	1 500	?	698(A$_1$)+798(B$_2$) = 1 496(B$_2$)
	1 595	A	2 × 798(B$_2$) = 1 596(A$_1$)
	1 645	A	2×830(ass. A$_2$-fund.); 798(B$_2$)+847 (ass.A$_2$)
	1 698	A	1 019(A$_1$) + 667(B$_1$) = 1 686(B$_1$)
	1 735	?	1 077(A$_1$) + 667(B$_1$) = 1 744(B$_1$)
a deutero furan	678	C	1 550(A′)−860(A″) = 690(A″)
	866	A	1 550(A′)−699(A′) = 851(A′)
	1 550	A	738(A″) + 815(A″) = 1 553(A′)
	1 636	A	2 × 815(A″) = 1 630(A′)
	1 671	A	815(A″) + 860(A″) = 1 675(A′)
	1 724	A	2 × 860(A″) = 1 720(A′)
β deutero furan	501	C	1 061(A′)−547(A″) = 514
	667	C	1 483(A′)−799(A″) = 684
	698	C	1 295(A′)−601(A″) = 694
	750	C	1 295(A′)−547(A″) = 748
	1 121	?	547(A″) + 601(A″) = 1 148(A′)
	1 444	A	2 × 720(A′) = 1 440(A′)
	1 529	A	729(A″) + 799(A″) = 1 528(A′)
	1 637-72	A	849(A″) + 799(A″) = 1 648(A′)
	1 696	A	2 × 849(A″) = 1 698(A′)

situated in the 830—850 cm^{-1} region. From this and the product-rule it follows that the product of the remaining frequencies must be (3.324-3.246) × 10^5. Since it is seen by comparison with the frequencies of the mono-deuterated species that one of the remaining frequencies may lie near 500 cm^{-1} it is a consequence that the third lie in the region 665—650. A value near 650 cm^{-1} fits nicely into the whole picture.

THERMODYNAMIC PROPERTIES OF FURAN

In their great paper on furan Guthrie *et al.*[7] have compared precalculated C_p- and entropy-values with experimental determinations. Guthrie has substantially chosen the same set of fundamental vibrational frequencies as ours with the exception of three. Instead of our frequencies at 550, 1 268, and 1 460 cm^{-1} Guthrie selected empirically frequencies at 700, 1 000, and

Table 7. Position of normal vibration frequencies for furan, a and β monodeutero furan, and a,a'dideutero furan. Frequencies in cm^{-1}.

	Furan	a-derivative		β-derivative	a,a'-derivative	
A_1	*ca.* 720	699	A′	*ca.* 720	698	A_1
	995	912		886	782	
	1 067	1 005		1 021	1 019	
	ca. 1 140	1 089		1 061	1 077	
	1 384	1 317		1 295	1 317	
	1 490	1 456		1 483	1 434	
	3 124	3 128		3 130	2 366	
	3 124	3 128		3 130	3 129	
B_1	874	805		829	667	B_1
	1 181	1 169		1 171	*ca.* 1 162	
	1 268	1 230		1 242	1 212	
	ca. 1 460	1 372		1 367	*ca.* 1 369	
	1 586	1 598		1 577	1 550	
	3 163	2 349		2 332	2 412	
	3 163	3 166		3 161	3 265	
A_2	550	515	A″	547	?	A_2
	660	657		646	?	
	1 030	860		849	?	
B_2	601	600		601	505	B_2
	744	738		729	678	
	838	815		799	798	

1 300 which brought the calculated thermodynamic functions (C_p° and S°) into best possible agreement with the experimental calorimetric data. In Table 8 the C_p-values found by Guthrie are compared with the ones, calculated by him and with the values calculated by us, using the same rigid-rotor, harmonic-oscillator approximation.

The agreement with experiment directly aimed at by Guthrie is definitely better than ours, especially at higher temperatures. Here, the rigid-rotor, harmonic-oscillator approximation is definitely too poor, since the assumption of harmonic vibrations is equivalent to assuming a too widely spaced

Table 8. Comparison between experimental and calculated C_p° values for furan (cal. deg.$^{-1}$mole^{-1}).

T. °K	317.25	358.20	402.20	449.20	487.20
C°_p (experim.)	16.80*W*.03	19.15	21.51	23.80	25.45
Calc. (Guthrie)	16.74	19.02	21.31	23.55	25.20
Calc. (B–B–H)	16.73	18.92	21.14	23.32	24.94

energy level pattern. It is not difficult to correct approximately for this at *low* temperature, say 317.25° K (Table 8). If roughly all observed frequencies are 1 % anharmonic, a "reduced" harmonic oscillator energy pattern may be introduced as shown in Fig. 1.

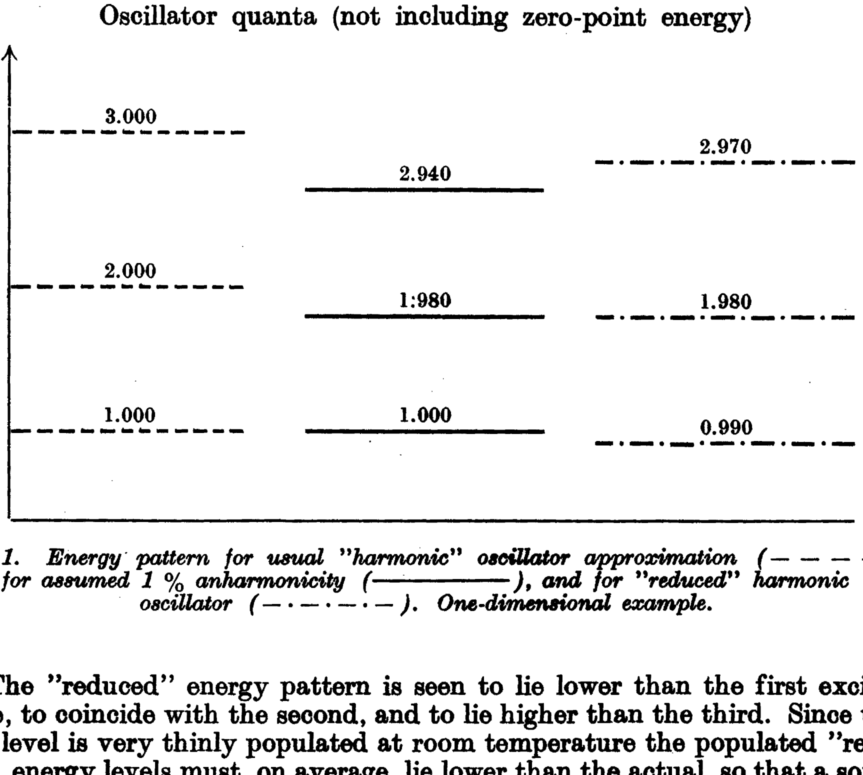

Fig. 1. Energy pattern for usual "harmonic" oscillator approximation (— — — —), for assumed 1 % anharmonicity (————————), and for "reduced" harmonic oscillator (— · — · — · —). One-dimensional example.

The "reduced" energy pattern is seen to lie lower than the first excited state, to coincide with the second, and to lie higher than the third. Since this last level is very thinly populated at room temperature the populated "reduced" energy levels must, on average, lie lower than the actual, so that a somewhat too ***high*** C°_p value should result from a calculation. By recalculation of the heat capacity at 317.25° K, using fundamental frequencies artificially lowered by 1 %, we calculate $C^\circ_p = 16.82$ cal. deg.$^{-1}$ mole^{-1}. This fits nicely with the experimental value (16.80). Unfortunately, this way of correcting cannot be applied at higher temperatures where the third, fourth *etc.* levels also become populated. The correction method given by Stockmeyer, Kavanagh, and Mickley [8] has been used for benzene by Scott *et al.*[9]. At nearly the same temperatures as those in Table 8 they found differences between observed and calculated C°_p values (using harmonic oscillator levels) of magnitude: 0.13; 0.17; 0.23; 0.36. Scott *et al.* showed that these differences could be identified with Stockmeyer's C_p -correction by adjustment of a single parameter. Since somewhat *smaller* differences may be expected in the case of furan, it is seen that it is hardly possible to bring our calculated C_p values in as fine a harmony with experiment as Guthrie *et al.* succeeded in obtaining. We are unable to explain the discrepancy. Guthrie *et al.* claim that "no group of (fundamental) frequencies including one below 600 cm^{-1} was found which gave reasonable agreement between calculated and observed thermodynamic properties". In order to agree with this statement we would have to abandon the idea of having "C"-type fundamentals in the spectra of the *mono*deuterated species at 515 and 547 cm^{-1} together with all the useful consequences for the interpretation of the whole spectral material derived from this.

In Table 9 we shall finally compare three experimental entropy values given by Guthrie *et al.*[7] with values calculated by him and his collaborators and values calculated by us, based on the new set of vibrational fundamentals.

Table 9. Comparison between experimental and statistical entropy values (in cal. deg.$^{-1}$ mole^{-1}).

T, °K	279.16	293.16	304.52
Experimental entropy	62.87±0.10	63.60	64.18
Calc. by Guthrie	62.86	63.60	64.19
» in this investig.	63.03	63.77	64.36

Our calculated entropy values are, therefore, about 0.17 entropy units too *high*. Due to experimental uncertainty the difference need not exceed 0.07 e.u. Perhaps this discrepancy can be explained by reference to Guthrie's paper. From the report of the experiments it follows that it could not be definitely excluded that furan did not form thermodynamically perfect crystals under the experimental conditions since a hysteresis in one of the transitions was noted.

A few values of the "reduced free energy" from our data are given in Table 10.

Table 10. Values of $-\left(\frac{G^\circ - H^\circ_0}{T}\right)$* *for furan in cal. deg.$^{-1}$mole^{-1}.*

T,° K	$-\left(\frac{G^\circ - H^\circ_0}{T}\right)$
273.16	53.16
298.16	54.02
300	54.07
400	57.25
500	60.20
600	63.01
700	65.72
800	68.31

The values of Table 10 deviate 0.06—0.10 cal deg.$^{-1}$ mole^{-1} from those given by Guthrie *et al.*[6].

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* $-\left(\frac{F^\circ - H^\circ_0}{T}\right)$ in American literature.

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