

The InfraRed Spectrum of Furan

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The absorptions at $\lambda 1700$ can possibly come from excitation of the non-bonding oxygen electrons to MO's of the σ type which are C—O or O—R antibonding. Particular assignments are difficult here since at short wave-lengths the number of transitions occurring in a given region may be large.

In the ion, transitions should occur in roughly the same regions as for the analogous transitions in the COOR group. However, the $N \rightarrow X$ absorption, which apparently is weak in the acids, is now expected to be very strong and probably explains the strong absorption below $\lambda 1900$ in the ion. A weak shoulder on the long wave-length

edge of this region indicates that the $N \rightarrow E_1$ absorption is present where it should be expected. The present state of information does not allow a distinction between configuration (2) and other possible configurations such as (3) to be made for esters.

In Fig. 3 these conclusions are summarized by an energy level diagram. A comparison of the positions of the corresponding states in $>C=O$, COOR, and COO^- is given in terms of correlations with the available experimental data.

In conclusion the writer wishes to express thanks to Professor R. S. Mulliken for much advice and encouragement.

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The Infra-Red Spectrum of Furan

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The infra-red spectrum of furan vapor has been investigated in the region from 500' to 35,000 cm^{-1} with a prism spectrograph using potassium bromide, rocksalt, and fluorite prisms. The data have been compared with those of other investigators and the frequency assignments proposed by Lord and Miller for pyrrole were applied to these data.

INTRODUCTION

THESE measurements of the infra-red spectrum of furan vapor were made several years ago in conjunction with an investigation of its ultraviolet spectrum which has been published.¹ Manzoni-Ansidei² has reported the measurement of the infra-red spectrum of liquid furan with a rocksalt prism spectrometer and his results will be shown later for comparison. Raman measurements have been made by a number of investigators³ with results which are consistent in the main. In spite of careful and extensive studies of the problem of the five-membered ring which have been made by Bonino and by Reitz,³ no conclusive explanation of the observed spectrum of furan has resulted.

Recently Lord and Miller⁴ have made an

analysis of the vibrational spectra of pyrrole based on Raman and infra-red measurements of pyrrole and several of its deuterium derivatives. Since the molecular structures of pyrrole and furan are so similar, it seemed of interest now to examine the furan data in the light of the frequency assignments made by Lord and Miller with the twofold purpose of interpreting the furan spectrum and of offering an independent test of these assignments.

EXPERIMENTAL

Preparation and Purification of Furan

Three samples of furan were used in these measurements. The first was kindly supplied by Professor G. B. Kistiakowsky and its preparation and careful purification for measurements of heats of hydrogenation have been described.⁵ A second was purchased from Eastman Kodak

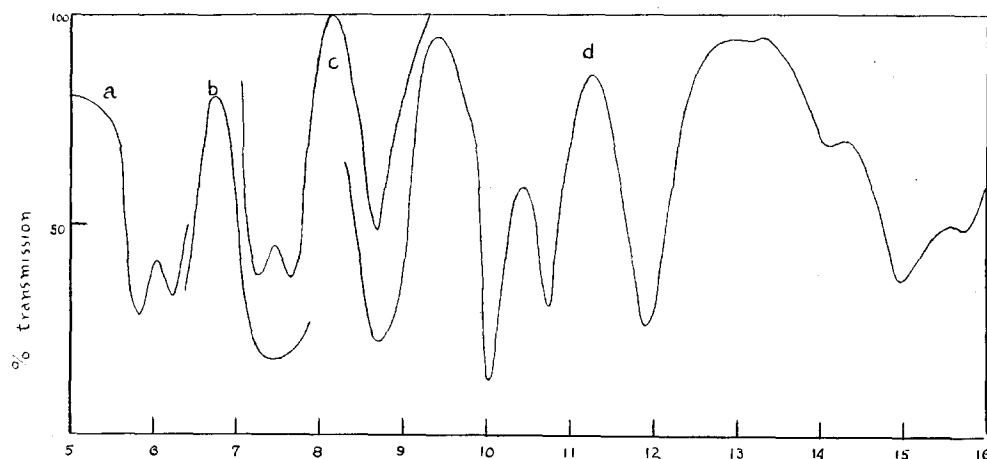
¹ L. Pickett, J. Chem. Phys. 8, 293 (1940).

² R. Manzoni-Ansidei and M. Rolla, Atti Accad. Lincei 27, 410 (1938).

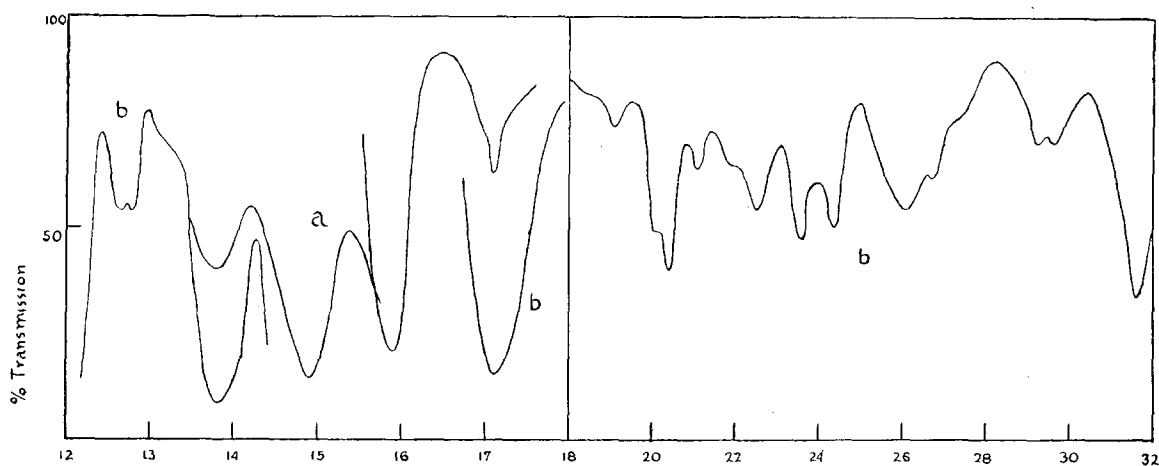
³ See F. Kohlrausch, *Der Smekel-Raman Effekt* (J. Springer, Berlin, 1938), p. 158, for bibliography.

⁴ R. C. Lord and F. A. Miller, J. Chem. Phys. 10, 328 (1942).

⁵ M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith, and W. E. Vaughan, J. Am. Chem. Soc. 60, 440 (1938).


 FIG. 1. Infra-red transmission curves for furan vapor. Wave numbers in 100 cm^{-1} .

	Pressure	Prism	Slit width
a.	101 mm	KBr	1.5 mm
b.	347 mm	KBr	1.5 mm
c.	30 mm	KBr	0.75 mm
d.	39 mm	NaCl	0.25-0.5 mm


 FIG. 2. Infra-red transmission curves of furan vapor using fluorite prism. *a*, pressure = 40 mm; *b*, pressure = 350 mm. slit width 0.1-0.35 mm. Wave number in 100 cm^{-1} .

Company and redistilled through a meter length fractionating column while the third was prepared as described in an earlier reference.¹ All three samples were used for the measurements with the fluorite prism. The first and third were studied with the rocksalt and the first with the potassium bromide prisms. The results obtained from all three were in agreement.

Infra-Red Measurements

The infra-red recording spectrometer at Harvard University which has been previously

described⁶ was used for the studies through the courtesy of Professor E. B. Wilson, Jr. The absorption of gaseous furan at pressures varying from 10 to 400 mm enclosed in tubes 30 cm long was determined over the region from 2.5 to 20μ using fluorite, rocksalt, and potassium bromide prisms in the appropriate regions of the spectrum. Certain improvements in the sensitivity and steadiness of the spectrometer, which made it possible to use a lower slit width and hence

⁶ H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. 6, 197, 247 (1938).

TABLE I. Frequencies observed for furan (in cm^{-1}).

Infra-red vapor	Infra-red liquid (M-A)	Raman (Reitz)
584 <i>s</i>	601 <i>vs</i>	601 <i>dp</i>
624 <i>s</i>	648 <i>w</i>	
725 <i>s</i>	740 <i>vs</i>	724 <i>p</i>
763 <i>s</i>		839 <i>dp</i>
872 <i>s</i>	864 <i>s</i>	871 <i>dp</i>
999 <i>vs</i>	990 <i>vs</i>	986 <i>p</i>
		1034 <i>dp</i>
1073 <i>s</i>	1052 <i>w</i>	1061 <i>p</i>
		1137 <i>p</i>
1189 <i>s</i>	1176 <i>m</i>	1171 <i>dp</i>
		1200 <i>p?</i>
1264 <i>w</i>	1249 <i>w</i>	1270 <i>dp</i>
1277 ?		
1387 <i>m</i>	1375 <i>m</i>	1380 <i>p</i>
		1457 ?
1490 <i>vs</i>	1495 <i>vs</i>	1483 <i>p</i>
1580 <i>s</i>		
1694 ?		
1712 <i>mw</i>		
1906 <i>w</i>		
2012 <i>vw</i>		
2040 <i>mw</i>		
2105 <i>w</i>		
2188 <i>vw</i>		
2246 <i>w</i>		
2360 <i>mw</i>		
2440 <i>mw</i>		
2604 <i>mw</i>		
2673 <i>w</i>		
2730 ?		
2915 <i>vw</i>		3089 <i>p</i>
2963 <i>vw</i>		3121 <i>p</i>
3164 <i>s</i>		3154 <i>p</i>

attain higher resolving powers, were made between the first and last measurements. Most of the curves presented were made with the improved apparatus except in the region below 800 cm^{-1} where the resolution with the potassium bromide prism was already excellent. At least four records were made of each part of the spectrum and these were in substantial agreement.

The transmission curves are given in Figs. 1 and 2; the positions of the bands observed are shown in Table I and for comparison, the values obtained by Manzoni-Ansidei from infra-red measurements of the liquid. The wave numbers of the Raman lines with their polarization properties as determined by Reitz⁷ are also given. The positions of the Raman lines show a somewhat wide variation as determined by different investigators and have been compared by Reitz.

DISCUSSION OF RESULTS

In comparing the present results with those of other reports, several points would seem to

require comment. The table shows that a considerable number of combination and overtone frequencies appear in the region investigated with the fluorite prism which have not been previously observed. Most striking however is the appearance of a strong absorption band at 1580 cm^{-1} . No band of this frequency has been observed in either Raman or infra-red measurements although a vibration frequency of about 1600 cm^{-1} is expected in all compounds with doubly-bonded carbon atoms and its apparent absence in furan has been the subject of much discussion.³ In the attempt to eliminate the possibility that the band observed here was due to an impurity, the three samples described above were all studied with the fluorite prism in this spectral region and all showed the same intense band. A plausible reason why such a band was not detected in the infra-red measurements made by Manzoni-Ansidei was found when the region was investigated with a rocksalt prism and is evident in Fig. 1. In this the band in question appears only as a shoulder on the side of the stronger band at 1490 cm^{-1} since the dispersion of the rocksalt prism is so much smaller than that of the fluorite in this region.

Two bands which appeared to be single at high pressures were seen to be clearly resolved into two heads each, when sufficiently low pressures were used. Thus the band reported by Manzoni-Ansidei at 601 cm^{-1} shows in these measurements two bands at 584 and 624 cm^{-1} while that at 740 has as its counterpart two at 725 and 763 cm^{-1} . These may be resolved branches of the same band or may represent separate bands.

The values of the present investigation are somewhat higher than those previously observed. The difference is probably to be attributed to the fact that these measurements were of furan vapor whereas all of the others were made on

TABLE II.

	Symmetry elements				No. of vibrations expected			Selection rules
	<i>E</i>	<i>C</i> ₂	σ_v^*	σ_z	Ring	C-H bend- ing	C-H stretch- ing	
<i>A</i> ₁	+	+	+	+	4	2	2	8
<i>A</i> ₂	+	+	-	-	1	2		3
<i>B</i> ₁	+	-	+	-	3	2	2	7
<i>B</i> ₂	+	-	-	+	1	2		3

* σ_v refers to molecular plane.

⁷ A. W. Reitz, Zeits. f. physik. Chemie **B38**, 275 (1938).

liquid furan. Crawford and Joyce⁸ have noted that in the case of methyl ether the vapor frequencies averaged 20 cm^{-1} higher than those of the liquid.

Assignment of Frequencies

The probable symmetry of the furan molecule is C_{2v} . Schomaker and Pauling⁹ have made electron diffraction measurements which give the molecular dimensions and support this view. The classification of frequencies to be expected on the basis of this symmetry is shown in Table II.

The C—H stretching frequencies are above 3000 cm^{-1} and are not resolved in these measurements as the dispersion of the spectrograph is low in this region. The vibrations of class A_2 are inactive in the infra-red and may thus be eliminated from consideration here, leaving fourteen frequencies to be identified.

Lord and Miller⁴ in their study of pyrrole and its deuterium derivatives have made assignments for all vibrations observed in their Raman and infra-red measurements and conclude that the assumption of C_{2v} symmetry accounts for the facts in satisfactory manner. Except for those frequencies associated with the N—H linkage, each fundamental vibration of pyrrole or pyrrole- $N-d$ would be expected to have its counterpart in the furan spectrum with some slight modification of frequency; there would also be differences to be taken into account because the pyrrole measurements were made in liquid state.

Table III gives the assignments proposed by Lord and Miller for pyrrole and in the last column corresponding assignments are made for furan. Such an assignment would account for all the observed bands except that at 584 which, as mentioned above, may be a resolved branch. There is no experimental evidence of three bands which would be expected but these may be

TABLE III.

Class	Vibration type	Pyrrole frequency	Furan frequency
A_1	ring	711	725
	ring	1144	1189
	ring	1384	1387
	ring	1467	1490
	C—H bending	1076	1073
	C—H bending	1237	1264
B_1	ring	647	624
	ring	1418	—
	ring	1530	1580
	C—H bending	1015	999?
	C—H bending	1046	—
B_2	ring	838	872
	C—H bending	768	763
	C—H bending	(1046)	—

superimposed on other bands. There is one serious difficulty in this interpretation, however, in that the Raman line at 986 (corresponding to the infra-red band for furan vapor at 999) was found by Reitz to be polarized⁷ and thus would represent a totally symmetrical vibration. Reitz' suggestion that the totally symmetrical ring vibrations in liquid furan have frequencies of 724, 986, 1137, and 1483 cm^{-1} is also supported by the finding of a parallel set of excited state frequencies in the ultraviolet spectrum,¹ where only the A_1 ring frequencies were likely to appear. Therefore the 999 cm^{-1} is thought to represent an A_1 ring frequency, probably concerning the oxygen atom to a large extent. In this case, 1387 cm^{-1} may represent a C—H bending vibration and 1264 cm^{-1} be a frequency of class B_1 .

It is possible to account for all of the bands observed above 1600 cm^{-1} as overtones or combinations which would be allowed by symmetry rules but the large number of existing possibilities mean that there is no great significance in such assignments.

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⁸ B. L. Crawford and L. Joyce, J. Chem. Phys. **7**, 307 (1939).

⁹ V. Schomaker and L. Pauling, J. Am. Chem. Soc. **61**, 1769 (1939).