represent vibrations of the ring. The structure of the corresponding band of cyclohexene is quite different with no vibrational frequencies of less than 250 cm.$^{-1}$ in evidence. However, a separation of 1485 cm.$^{-1}$ is clearly marked and doubtless corresponds to the double bond stretching frequency of 1650 cm.$^{-1}$ observed in the ground state through Raman and infrared measurements. In cyclohexene as in cyclohexane no prominent separation was observed which might parallel the ring breathing frequencies near 800 cm.$^{-1}$ which cause strong polarized Raman lines.[18]

(5) The intensity data for benzene give an opportunity for the testing of some of the controversial assignments. The band system at 50,000 cm.$^{-1}$ consists of a group of bands with a prominent separation of around 800 cm.$^{-1}$ representing a ring-breathing vibration. The first of these bands seems to be rather a group of three narrow bands and is of lower intensity as is the first band of the forbidden transition in the quartz ultraviolet. However, the intensity is not sufficiently different from the others to warrant a conclusion that it originates from a higher vibrational level of the ground state.

This conclusion was supported by a study of the spectrum of benzene vapor in a jacketed tube maintained near -20°. The relative intensity of the first two bands showed no measurable change from that at room temperature. Studies at lower temperatures were not feasible because of condensation of benzene.

The f value for this band measured from 47,500–53,750 cm.$^{-1}$ was calculated as 0.12. Platt and co-workers[14] found an f value of 0.1 for the corresponding band in heptane solution which seems to be displaced toward the visible by about 1000 cm.$^{-1}$. The band system at longer wave lengths undergoes a much smaller shift from vapor to solution. Both the position and the intensity of the most intense band seem quite different in vapor and in the solution measurements cited,[14] which would indicate that the solvent has a larger effect on this band than on those of longer wave length. The top of the underlying band is at an E value of about 80,000 while the strong peak at 55,870 cm.$^{-1}$ extends even higher. An over-all value of f from 53,750 to 60,000 cm.$^{-1}$ was calculated as 1.23 though this is believed to represent two transitions, one a Rydberg series overlying an N–V transition of type A_{1g}–E_{1u}.

The next papers of this series will discuss five- and six-membered ring compounds containing oxygen and nitrogen atoms, respectively.

Acknowledgment.—The authors are indebted to the Office of Naval Research, and also to the Research Corporation for the Beckman spectrophotometer used in some of the measurements.

SOUTH HADLEY, MASS. RECEIVED APRIL 25, 1951

[18] K. W. F. Kohlrausch and H. Wittek, *Z. physik. Chem.*, **B48**, 177 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MOUNT HOLYOKE COLLEGE]

The Vacuum Ultraviolet Absorption Spectra of Cyclic Compounds. II. Tetrahydrofuran, Tetrahydropyran, 1,4-Dioxane and Furan[1]

BY LUCY W. PICKETT, NANCY J. HOEFLICH AND TIEN-CHUAN LIU

The vacuum ultraviolet absorption spectra have been measured for four cyclic ethers, tetrahydrofuran, tetrahydropyran, 1,4-dioxane and furan in vapor phase. Bands are found for each of the compounds in the region between 50,000 and 60,000 cm.$^{-1}$ which are due to the excitation of the unshared electrons of oxygen. In the case of the first three compounds characteristic structure showing low frequency vibrational differences is prominent in these bands. Though the first three compounds have only low absorption at wave numbers below 50,000 cm.$^{-1}$, furan shows the broad absorption band characteristic of dienes in this region.

Introduction

An earlier paper of this series[2] discusses the spectra of five- and six-membered saturated hydrocarbon rings and the effect on the absorption of introducing unsaturation electrons in the ring in the form of one or multiple double bonds. In this paper the effect of unsaturation electrons present as unshared electrons of one or more oxygen atoms is considered. The cyclic ethers tetrahydrofuran and tetrahydropyran were chosen since they have an oxygen atom in an otherwise saturated five- and six-membered ring, respectively, while 1,4-dioxane illustrates the effect of two oxygen atoms which are sufficiently separated to have little effect on each other. In furan there are unsaturation electrons from the carbon atoms of the ring to give a conjugated system.

There has been little or no investigation of the vacuum spectra of the first three compounds. That of furan has been previously reported by Pickett[3a] and by Price.[3b] Measurements of a related compound, dihydropyran,[4] in solution have shown only a broad band with a maximum value of E of 3,800 at 51,280 cm.$^{-1}$.

Experimental

The spectral measurements were made as described in the first paper of this series.[2,5] All samples used were purified in this Laboratory and distilled in an atmosphere of nitrogen

---

[1] This work was supported by the ONR. Contract N8-onr-74100; NR-055-160. This paper was presented at the Physical and Inorganic Section of the 119th Meeting of the American Chemical Society, April, 1951.

[2] L. W. Pickett, M. Muntz and E. M. McPherson, THIS JOURNAL, **73**, 4862 (1951).

[3] (a) L. W. Pickett, *J. Chem. Phys.*, **8**, 293 (1940); (b) W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* (*London*), **A179**, 201 (1941).

[4] J. R. Platt, H. B. Klevens and W. C. Price, *J. Chem. Phys.*, **17**, 466 (1948).

[5] A. J. Harrison, C. Gaddis and E. M. Coffin, *ibid.*, **18**, 221 (1950).

immediately before use. All measurements were made on flowing vapors.

Tetrahydrofuran.—Tetrahydrofuran samples from three sources were used. The first, Sample I, was purchased from Eastman Kodak Co., dried over calcium sulfate and metallic sodium, and distilled fractionally through a 30-cm. Fenske column packed with glass helices. A test for peroxide proved negative and the color of a drop of bromine solution remained for about twenty minutes. The fraction used boiled at 66.0°, n^{21}_{D} 1.4066.

Because of the unique appearance of the spectrum and the possibility that impurities might be present, two samples were prepared by catalytic hydrogenation of furan.[6] First a solution of 46 g. of furan (prepared by heating furoic acid) in 61 g. of redistilled tetrahydrofuran as solvent was hydrogenated using a Universal Oil Products nickel catalyst. A temperature slowly rising to a maximum of 180° in 15 hours and a maximum pressure of 1600 lb. were used. The product distilled constantly and the first and last fractions had the same refractive index. The product was dried with calcium sulfate and sodium and distilled through a Fenske fractionating column in a nitrogen atmosphere. A middle portion which boiled at 66.0° at 755 mm. pressure was used for the spectral studies. The agreement of the spectra of the two samples is shown in Table I which gives values of log E at the top of the band.

TABLE I

VALUES OF LOG E AT TOP OF ABSORPTION BAND FOR DIFFERENT SAMPLES OF TETRAHYDROFURAN

Wave number in cm.$^{-1}$	log E Sample 1 pressure, 0.169 mm.	Sample 2 pressure, 0.168 mm.
57,795	3.40	3.39
57,880	3.42	3.40
57,970	3.42	3.41
58,020	3.43	3.43
58,075	3.42	3.41
58,115	3.42	3.43
58,150	3.42	3.42
58,200	3.42	3.43
58,240	3.40	3.40
58,290	3.40	3.40
58,330	3.39	3.39
58,590	3.40	3.40
58,425	3.38	3.39
58,595	3.35	3.35

A third sample was prepared from the hydrogenation of 100 g. of furan without solvent for eight hours at a maximum pressure of 2000 lb. and a maximum temperature of 150°. Since the first plate of this showed agreement with those of the first two samples, no further measurements were made.

Tetrahydropyran.—The tetrahydropyran used for the first series of measurements was obtained through the courtesy of the du Pont Co. A sample purchased from Halogen Chemical Co. was used for a second set of measurements. Both samples were dried over calcium sulfate and refluxed and distilled from sodium (b.p. 88.0° at 734.3 mm., n^{24}_{D} 1.4197).

Both samples were found to be contaminated with very slight traces of benzene which was identified and analyzed through the characteristic absorption bands near 38,000 cm.$^{-1}$ where the tetrahydropyran is transparent. Since the absorption coefficient of the latter is not known, the calculation could not be exact but the benzene was estimated at 0.005% from the spectrum. Some attempts were made to remove this by passing the tetrahydropyran through a graphon column.[7]

This treatment lowered the proportion of benzene but did not eliminate it. It was felt that so small a proportion of benzene would have a negligible effect on the spectrum of tetrahydropyran and this view was supported by the fact that the most intense band of benzene at 55,870 cm.$^{-1}$ could not be observed.

Dioxane.—Several samples of dioxane were used. One supplied by Eastman Kodak Co. was dried over sodium 12 hours, refluxed 15 hours over fresh sodium and fractionally distilled in an atmosphere of nitrogen. The fraction boiling at 101.0 ± 0.1° was used for the measurements. Treatment with hydrochloric acid, to remove possible aldehyde

TABLE II

OSCILLATOR STRENGTH OF BANDS

Substance	Wave number, cm.$^{-1}$	f value
Tetrahydrofuran	50,000–55,500	0.012
	55,500–61,800	.041
Tetrahydropyran	51,500–54,300	.008
	54,300–60,500	.085
Dioxane	52,200–60,510	.11
Furan	45,000–51,800	.12
	51,800–57,900	.078

TABLE III

w = weak, m = medium, s = strong, d = doublet or group of unresolved bands

Wave numbers of bands × 10^{-1} cm.$^{-1}$ (Waves per mm.)

Tetrahydrofuran

Group 1	Group 2		Group 3
5012w	5144m	5331s	5564s
5019w	5163ms	5343w	5584s
5026w	5171m	5352ms	5603w
5036w	5183ms	5365w	5610s
5044w	5190m	5373m	5628s
5053w	5203s	5386mw	5650s
5062w	5212m	5394m	5670s
5073w	5225s	[a]5414w	5690s
5085w	5248s	5435dw	[b]5712s
5096m	5268s	5455dw	
5106w	5288s	5472dw	
5115w	5300w	5492dw	
5126dw	5309s	5512dw	
5136w	5322w	5534dw	

Tetrahydropyran

Group 1		Group 2	
5167w	5289ms	5444s	5643s
5188w	5295m	5460w	5655w
5193s	5309w	5483ms	5679ms
5209w	5313ms	5488ms	5713m[b]
5213w	5321m	5494s	
5217ms	5334	5519w	
5230ms	5338dm	5527m	
5237mw	5346mw	5537s	
5242ms	5360m	5547m	
5256mw	5369mw	5572s	
5264s	5384mw	5599m	
5274m	5392w	5614s	
5283w	5418w[a]	5633w	

Dioxane

5038wd	5170mw	5271s	5389ms
5098w	5193w	5291ms	5405s
5110w	5203wd	5316s	5416m
5119w	5232ms	5345ms	5435m
5153mw	5238mw	5365s	5459m
5163mw			

[a] Band may be present covered by Hg absorption line; [b] Bands beyond this point diffuse.

---

(6) The hydrogenation was carried out by Dr. A. J. Harrison and Eileen Tannenbaum.

(7) This was supplied by Godfrey L. Cabot, Inc., through the courtesy of Dr. Ralph Beebe of Amherst College. The procedure was modified from that used by Dr. Beebe and J. P. Butler.

and acetal impurities[8] did not have any apparent effect on the spectrum.

Furan.—The furan used had originally been prepared by Dr. G. B. Kistiakowsky[9] and kept in vacuum. This was distilled before use.

Results

The absorption curves are shown in Figs. 1 and 2. Tetrahydrofuran, tetrahydropyran and dioxane are seen in Fig. 1, successively displaced upward by log E 0.5 since they overlap to a considerable extent. The scale for each is indicated under the appropriate letter at the left of the figure. The regions dotted are shown in this way because lines in the light source mean that the structure is uncertain. Furan and tetrahydrofuran are compared in Fig. 2.

The oscillator strengths of the four compounds, calculated $f = 4.32 \times 10^{-9} \int E d\nu$, are shown in Table II. The positions of the bands of three compounds are given in Table III. The uncertainty is ±20 cm.$^{-1}$. Those of furan have been published.[3a,3b]

Discussion

It is apparent that all three compounds containing oxygen in an otherwise saturated ring show absorption in the same range of the spectrum, namely, from 50,000–60,000 cm.$^{-1}$. It was not possible to get high enough vapor pressure in the absorption cells to measure the absorption below 50,000 cm.$^{-1}$, but it seemed to fall off rapidly. Measurements of the liquids with the Beckman spectrophotometer showed that these compounds are practically transparent below 40,000 cm.$^{-1}$. There is a slight increase in absorption above this point but the molecular extinction coefficient remains below 1 throughout the region observed (to 44,000 cm.$^{-1}$). This region is extraordinarily sensitive to minute traces of impurity so that the very slight absorption observed could be due to this cause. It is certain that there are no allowed transitions of any of these substances at wave numbers below 50,000 cm.$^{-1}$. There is in each case a region of relative transparency between 60,000 and 62,000 cm.$^{-1}$ followed by another strong band whose maximum is beyond 64,000 cm.$^{-1}$.

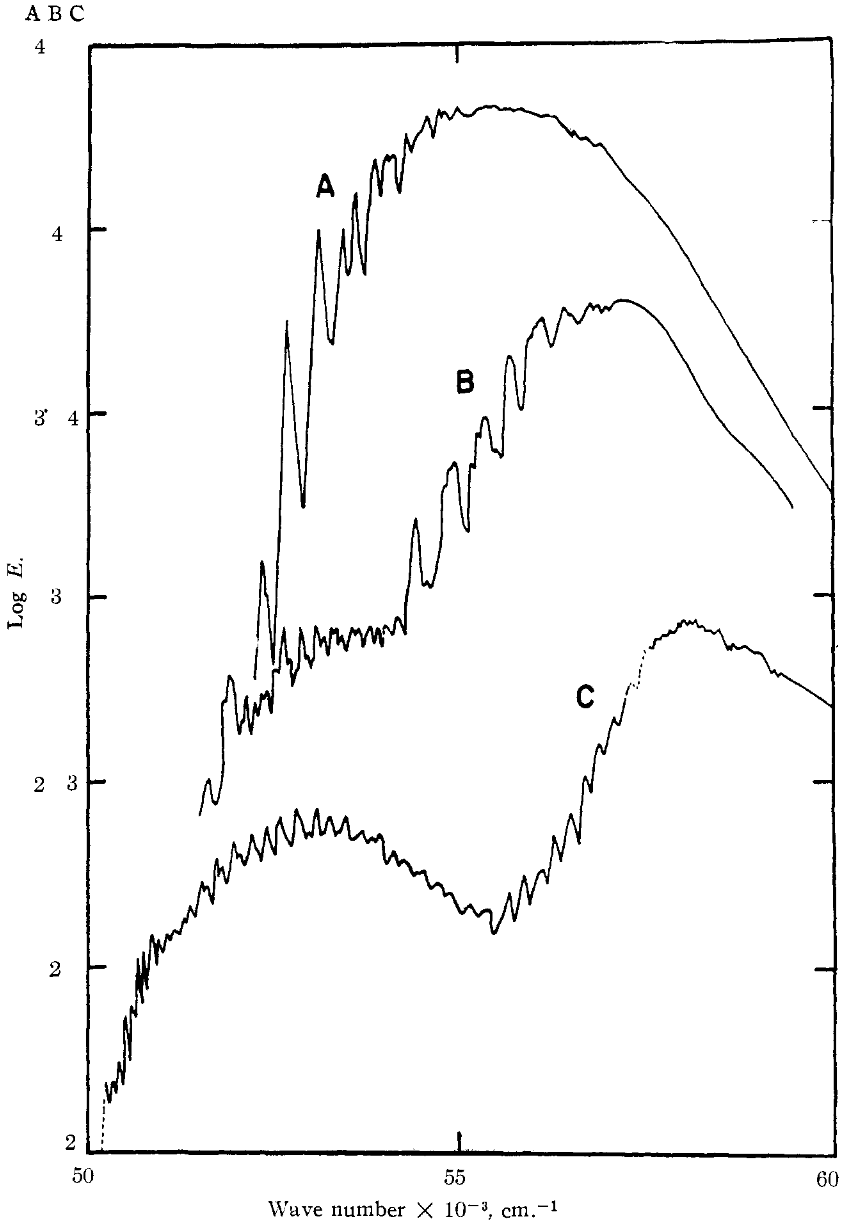

Fig. 1.—Absorption curves of: A, dioxane; B, tetrahydropyran; C, tetrahydrofuran.

In the region of characteristic absorption, the three saturated compounds all have absorption bands of moderate intensity, characterized by prominent vibrational structure. In the case of the five-membered ring compound there are two clearly marked bands, whereas in the six-membered ring compound these seem to be displaced toward each other, and in the dioxane there would seem to be one band only, which may represent a superposition of two bands. Since cyclohexane and cyclopentane[2] do not absorb in this region and since diethyl ether[10] has two bands comparable in position to those of tetrahydrofuran, it is evident that these bands may be attributed to excitations of the non-bonding electrons of the oxygen atom in each case.

The intensity of the bands increases for the three compounds, tetrahydrofuran, tetrahydro-

---

(8) This purification was carried out by Dr. George Hall of this Laboratory according to the process described in Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 369.

(9) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith and W. E. Vaughan, THIS JOURNAL, **60**, 440 (1938).

(10) G. Scheibe and H. Grieneisen, *Z. physik. Chem.*, **B25**, 52 (1934).

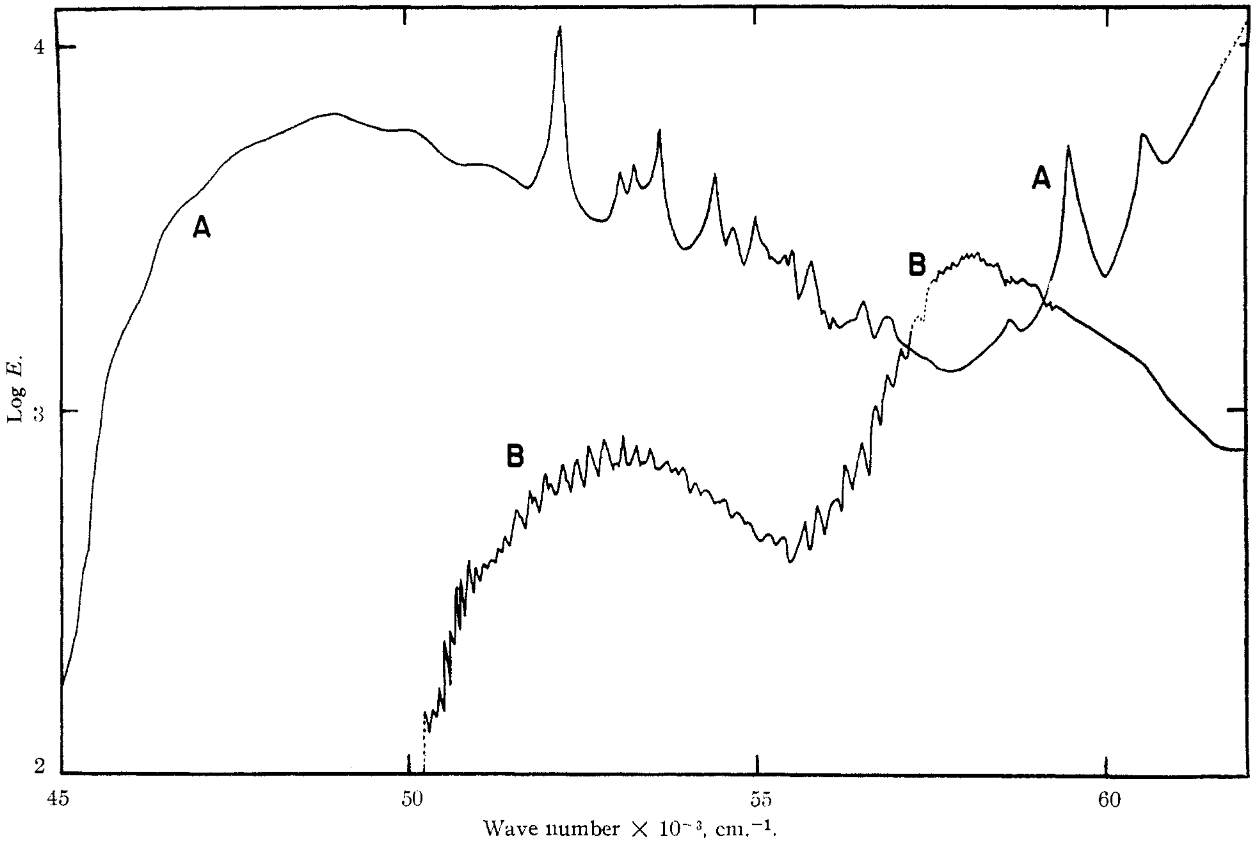

Fig. 2.—Absorption curves of: A, furan; B, tetrahydrofuran.

pyran and dioxane. The first band in the case of the first two compounds is much less intense than the second. It would appear from Table II that the oscillator strength of a band resulting from an oxygen atom in a saturated ring is below 0.1. In the case of dioxane, where the presence of two oxygen atoms would be expected to increase the transition probability twofold as a first approximation, the oscillator strength is larger but not twice as great as for the tetrahydropyran. All these values are well below the range of those found for cyclopentene and cyclohexene where the excitation is that of the π electrons of the double bond.

A striking characteristic of all three compounds is the prominent structure of closely spaced narrow bands listed in the tables. Those of tetrahydrofuran present an especially interesting pattern. The approach to the lower frequency band is marked by sharp bands of low intensity with separations of 80–120 cm.$^{-1}$. There may be others at pressures greater than those attainable here. Beginning at 51,440 cm.$^{-1}$ is a fairly strong band followed by a long progression of saw-toothed doublets. These can be accounted for on the basis of an excited state vibration of 205 cm.$^{-1}$ and one of 275 cm.$^{-1}$ with long progressions of the former. Some low temperature measurements were made in order to confirm these assignments but were inconclusive because of condensation of the tetrahydrofuran vapor.

Kohlrausch and Reitz[11] have observed low intensity bands at 215 and 276 cm.$^{-1}$ in the Raman spectrum of tetrahydrofuran. Such a low frequency vibration must be a ring puckering motion and, because of its prominence in the ultraviolet spectrum, doubtless represents a wagging of the oxygen atom in particular. The more intense band system of tetrahydrofuran has its first strong maximum at 55,640 cm.$^{-1}$ and a fairly regular progression of bands of spacing 200 cm.$^{-1}$ which becomes diffuse after the first nine bands.

There seem to be two well-marked band systems of tetrahydropyran. The first beginning at 51,930 cm.$^{-1}$ would account for 17 of the 25 observed bands on the basis of a ground state vibration of 280 cm.$^{-1}$ and an excited state vibration of 240 cm.$^{-1}$ ($\gamma = 51930 + v'\ 240 - v''\ 280$ where $v'' = 0.1$ and $v' = 0 - 8$)—while others may be explained as combinations with 810 cm.$^{-1}$ frequency. The second transition of higher intensity has the first strong band at 54,440 cm.$^{-1}$. The separations here are larger and the pattern not as clearly defined.

The first bands of dioxane (which are shown in the table but not on the figure) have a triplet structure. In some cases this could not be clearly resolved and the position of the band group is given. The values of molecular extinction coefficient showed more variation with pressure than in any of the other compounds and hence are less reliable. This is believed to be due to the intensity of the individual bands which characterize the slope of the absorption band.

The spectra of these three molecules thus differ

---

(11) K. W. F. Kohlrausch and A. W. Reitz, *Z. physik. Chem.*, **B45**, 249 (1939).

somewhat in the position and apparent number of bands and in the fact that tetrahydrofuran and tetrahydropyran are characterized by long progressions of bands of 200 cm.$^{-1}$ separation while these are absent in dioxane. To account for these differences one might reasonably look at the symmetry of the different molecules and at the bond angle of the oxygen atom in each. Electron diffraction studies[12] and infrared[13] and Raman data have indicated that dioxane exists wholly or mainly in a chair form of symmetry C_{2h} while it is obvious that the other molecules lack a symmetry center. Thus, quite different selection rules would hold and transitions from an unexcited to an A_g or B_g state would be forbidden for dioxane while analogous changes in the other molecules would be allowed. This may be the explanation of the fact that dioxane has one absorption band in this region while the others have two. The vibrational pattern is explicable on the basis of symmetry since the low frequency out-of-plane vibrations around 200 cm.$^{-1}$ which have been found or predicted[13] for these molecules would be totally symmetrical and hence occur with an allowed electronic transition only in the case of the less symmetrical molecules, tetrahydrofuran and tetrahydropyran, while in the dioxane they would be expected only in doubled quanta. Separations about 450 cm.$^{-1}$ are to be noted in the spectrum of this compound. Ramsay[13] has concluded from the vibration spectrum of this molecule that there is a center of symmetry and has identified totally symmetrical vibrations of 485, 834 and 1111 cm.$^{-1}$. The first is believed to be an out-of-plane vibration and the second a breathing vibration.

The bond angles of tetrahydrofuran, dioxane and dimethyl ether all seem to be close to the tetrahedral angle from electron diffraction experiments,[12,14] while that of tetrahydropyran has not been published. While the bond angle may be expected to be a factor in the ease of excitation of the electrons, no correlation can be made at present.

The absorption curve for furan has been published before.[3a] The present investigation included a remeasurement of the compound since the methods of measuring intensity have improved but no marked changes were found. The spectrum of this compound is quite different from those of the other three as would be expected from its structure. The broad diffuse bands between 45,000 and 52,000 cm.$^{-1}$ are characteristic of dienes. The system characterized by sharp bands begins at the same region as in the saturated compounds but is of much greater intensity. The pattern has been analyzed and shows a correspondence with the symmetrical ring vibrations found in Raman spectra. The point of emphasis here, however, is that the vibrations of about 200 cm.$^{-1}$ found in the saturated ethers are missing here. Furan is probably a planar molecule of C_{2v} symmetry and a wagging motion of the oxygen would be non-totally symmetric in this molecule. Thus it would appear only in doubled quanta in the electronic spectra.

In furan a separation attributable to a ring breathing mode of vibration has been identified in the band system beginning at 52,220 cm.$^{-1}$. However, in the saturated ethers there is no evidence of a prominent separation between 550 and 900 cm.$^{-1}$. At first sight this was surprising because in the Raman spectra of these compounds,[11,15] there is a prominent polarized line of 800–900 cm.$^{-1}$ due to a totally symmetrical ring breathing vibration and in general totally symmetrical vibrations appear in the excited state with somewhat modified frequency. The conclusion from the facts would be that such a vibration is not disturbed by the electronic excitation which is localized on the oxygen atom in the case of the saturated ethers. The bands doubtless represent first members of Rydberg series leading to ionization of one of the unshared electrons of the oxygen atom.

It may be worthy of note that the second band in the case of the tetrahydrofuran is displaced to higher frequencies than that of tetrahydropyran. Cyclopentane is similarly displaced with respect to cyclohexane.

SOUTH HADLEY, MASS. RECEIVED APRIL 25, 1951

---

[12] L. E. Sutton and L. O. Brockway, THIS JOURNAL, **57**, 473 (1935).

[13] D. A. Ramsay, *Proc. Roy. Soc.* (*London*), **A190**, 562 (1947).

[14] J. Y. Beach, *J. Chem. Phys.*, **9**, 54 (1941).

[15] L. Kahovec and K. W. F. Kohlrausch, *Z. physik. Chem.*, **B35**, 29 (1937).