The Long WaveLength Spectra of Saturated Carboxylic Acids, Esters, and Salts

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Electron configurations for the low excited states of the COOR radical (R = alkyl group or H atom) and the COO⁻ ion are given. Their longest wave-length absorptions are interpreted in terms of transitions to their lowest excited states. In the COOR radical this absorption comes at λ2100 and is weak. It is interpreted as due to a transition like that producing the weak region at λ2900 in the spectrum of the >C=O group in aldehydes and ketones. The COO⁻ ion appears to show an analogous weak absorption but this is largely covered by a much stronger region. The latter is interpreted as possibly due to a transition in which a non-bonding oxygen electron is excited to an antibonding molecular orbital of the unsaturation or x type. This transition should be strong in the ion, probably is weak in the acids and esters, and is entirely absent in the aldehydes and ketones. Possible interpretations of the λ1700 absorption in acids and esters are briefly discussed.

I. INTRODUCTION

THE longest wave-length absorption regions characteristic of saturated molecules containing the >C=O, COOR, and COO⁻ groups are shown in Fig. 1. In all saturated carboxylic acids and esters there is a weak region with a maximum near λ2100.[1-3] Since the absorption must arise from parts of the molecules having nearly identical electronic structures, it can be attributed to the carboxyl group. One is also led to expect such a weak absorption at long wave-lengths for the carboxyl group, since the longest wave-length absorption from the carbonyl (>C=O) group at λ2900 is weak.[4]

In the acids and esters the weak absorption merges into a stronger region with a maximum near λ1700.[1] This absorption is ten or more times stronger than that at λ2100.[5]

The spectrum of the carboxyl ion can be obtained by dissolving the easily ionized alkali salts of the saturated acids in water.[2,6] The absorption then begins at somewhat shorter wave-lengths than for the acids and rises rapidly without showing any maximum within the range

[1] G. Scheibe, F. Povenz, and C. F. Linström, Zeits. f. physik. Chemie **B20**, 297 (1933).

[2] H. Ley and B. Arends, Zeits. f. physik. Chemie **B17**, 177 (1932).

[3] J. Bielecki and V. Henri, Ber. d. D. Chem. Ges. **46**, 1304 (1913).

[4] See H. L. McMurry, J. Chem. Phys. **9**, 231 (1941) for a discussion.

[5] The f values for the λ1700 and λ2100 absorptions in the vapor as estimated from the curves of Scheibe *et al.* (reference 1, Fig. 7) come out about 0.02 and 0.002, respectively. The f value for the λ2100 absorption of the pure liquids or the solutions of the compounds is also about 0.002 (reference 2). The absorption curves for the λ1700 regions have not been measured beyond their maxima. The estimated f value, which depends on the width of the region at half the maximum intensity, is less reliable for the λ1700 regions than for the others. See reference 4 for the method of estimating f values.

[6] Although the ionization constants for the acids are small, an appreciable number of carboxyl ions can be obtained in very dilute water solutions of these materials. With long path lengths their absorptions should be like those of the salts. Formic and succinic acids have relatively high ionization constants and should be suitable for such an experiment. Experiments like this have been done with salicylic acid (a conjugated acid). See C. Shin-Piaw and C. Fabry, Comptes rendus **208**, 292, 1563 (1939).
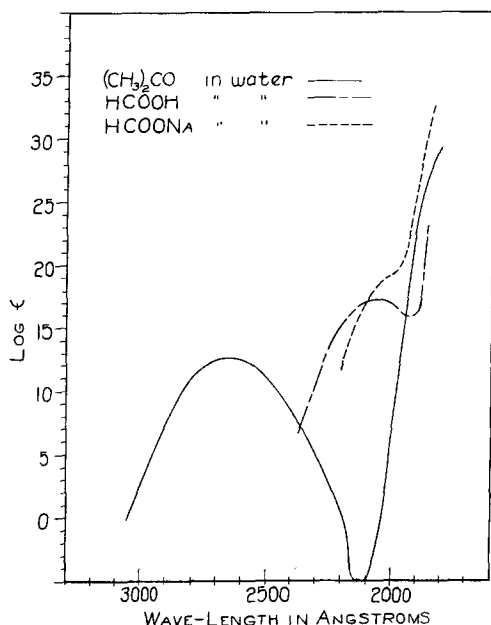
FIG. 1. Absorption regions characteristic of the $>C=O$, COOR, and COO^- groups. These curves are based on data and absorption curves given by Ley and Arends in reference 2 and also in Zeits. f. physik. Chemie **B12**, 132 (1931). In the vapor the HCOOH absorption below $\lambda 2000$ shows a maximum around $\lambda 1700$ where log $\epsilon = 3.0$ (see reference 1).

of observations.[2] The curves (see Fig. 1) suggest that this absorption may have a higher intensity than the $\lambda 1700$ region in the acids. Its maximum is very possibly at somewhat longer wave-lengths than $\lambda 1700$. The spectra of the ions obtained from several salts show a low intensity shoulder on the long wave-length side of this strong region. Apparently this weak transition, if it is an independent one, has its maximum at shorter wave-lengths than $\lambda 2100$.

In the following work the electronic structures and spectra of saturated molecules containing the COOR radical or the COO^- ion will be discussed. A similar discussion for molecules in which this radical or ion is conjugated to the rest of the molecule is contemplated for a later article.

II.   ELECTRONIC STRUCTURE OF THE COO^- ION AND THE COOR RADICAL IN SATURATED ORGANIC MOLECULES

A. Electron Configurations for the COO^- Ion

The semilocalized molecular orbitals (MO's) for the COO^- ion must belong to representations

of the point group[7,8] C_{2v}. Those MO's which are important for the present discussion have forms which may be determined qualitatively by solving the secular equations[9] from which they are derived. They can be described in terms of the axes shown in Fig. 2.

Three types of MO's must be considered. One of these, the "x" type,[10] contains a node in the plane of the group and can be approximated by linear combinations of the $2p_x$ atomic orbitals (AO's) of the three atoms. There are three x MO's denoted here by $\chi_1(b_1)$, $\chi_2(a_2)$, and $\chi_3(b_1)$, where the letters b_1 and a_2 refer to the species of C_{2v} to which the MO's belong. The solutions of the secular equation for these MO's show that χ_1 is $O-C-O$ bonding, χ_2 is non-bonding, and χ_3 is $O-C-O$ antibonding.[11] The second group of
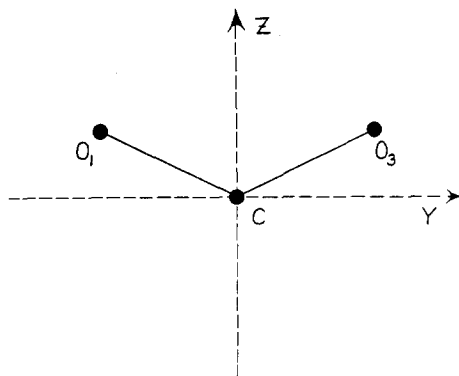

FIG. 2. Axes for COO^-. See reference 8 for details.

[7] See R. S. Mulliken, Phys. Rev. **43**, 279 (1933).

[8] The OCO angle in acids and esters is about 125°, the $C-O$ distances are reported to be about 1.29A. The dimensions in the ion should not be greatly different. See L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1939), p. 188.

[9] If an MO is expressed as a linear combination of all the atomic orbitals (AO's) of the valence electrons in the atoms concerned, a secular equation can be formed by the usual methods of perturbation theory. For atom groups of high symmetry this equation factors into parts each of which gives the forms and energies of the MO's belonging to a particular symmetry class.

[10] H. L. McMurry, J. Chem. Phys. **9**, 241 (1941).

[11] The χ MO's may be expressed by the relation

$$\chi_i = a_i x_1 + b_i x_2 + c_i x_3,$$

where

$$a_1 = c_1 > b_1; \quad a_2 = -c_2; \quad b_2 = 0; \quad a_3 = c_3 \gtrless -b_3.$$

An MO formed as a linear combination of AO's (LCAO MO) is bonding between two atoms when the positive parts of the AO's of adjacent atoms overlap. It is antibonding when positive and negative parts overlap. These bonding characteristics are weak, essentially non-bonding, whenever the overlapping of adjacent AO's is small, or when one or both AO's appear with a small coefficient in the LCAO expression (see reference 9).

MO's are of the "σ" type with wave functions concentrated along the $O-C$ lines. These can be built by combining suitably oriented $2p$ AO's of the O atoms with properly chosen mixtures of $2p_z$, $2p_y$, and $2s$ AO's of carbon. Two of these MO's designated as $\varphi_1(a_1)$ and $\varphi_2(b_2)$ are $O-C$ bonding while two others, $\psi_1(a_1)$ and $\psi_2(b_2)$, are $O-C$ antibonding.[12] Finally, there are two MO's, denoted here by $\omega_1(a_1)$ and $\omega_2(b_2)$, which are expected to exhibit the same non-bonding character that distinguishes the closely analogous y_0 MO in aldehydes and ketones.[4] They can be

constructed primarily from $2p$ AO's of the O_3 and O_1 atoms with symmetry axes in the plane of the molecule perpendicular to the O_3-C and O_1-C lines, respectively.[14] These oxygen AO's will hereafter be denoted by q_3 and q_1, respectively.

The electron configurations for the normal and low excited states of the COO^- ion are given below in what is later estimated to be the order of increasing energy. The species symbol is used wherever an MO appears.

$$
\begin{aligned}
N&-\varphi_1{}^2(a_1) \quad \varphi_2{}^2(b_2) \quad \chi_1{}^2(b_1) \quad \omega_1{}^2(a_1) \quad \chi_2{}^2(a_2) \quad \omega_2{}^2(b_2), & {}^1A_1. \\
E_1&-\varphi_1{}^2(a_1) \quad \varphi_2{}^2(b_2) \quad \chi_1{}^2(b_1) \quad \omega_1{}^2(a_1) \quad \chi_2{}^2(a_2) \quad \omega_2(b_2) \quad \chi_3(b_1), & {}^{3,1}A_2. \\
X&-\varphi_1{}^2(a_1) \quad \varphi_2{}^2(b_2) \quad \chi_1{}^2(b_1) \quad \omega_1{}^2(a_1) \quad \chi_2(a_2) \quad \omega_2{}^2(b_2) \quad \chi_3(b_1), & {}^{3,1}B_2. \\
E_2&-\varphi_1{}^2(a_1) \quad \varphi_2{}^2(b_2) \quad \chi_1{}^2(b_1) \quad \omega_1(a_1) \quad \chi_2{}^2(a_2) \quad \omega_2{}^2(b_2) \quad \chi_3(b_1), & {}^{3,1}B_1.
\end{aligned} \tag{1}
$$

In aldehydes and ketones the lowest excited MO is of the x type.[4,10] This has also been assumed to be true for the analogous χ_3 MO in (1). The ω_1 MO is possibly slightly $O-C-O$ bonding and has been placed lower than the χ_2 MO which is almost entirely localized on the oxygen atoms[11] and therefore must be almost completely non-bonding. The evidence discussed below makes it seem probable that the absorption at longest wave-lengths in the ion can come only from excitation of either an ω_1 or an ω_2 electron. For this reason ω_2 has been given the highest energy of any MO used in (1). It is probably slightly antibonding.

The longest wave-length absorption in the ion[2] has a strong maximum below $\lambda 1850$ and carries a shoulder on its long wave-length side indicating that a weak region possibly is present around $\lambda 1900-\lambda 2000$. These features can be explained in terms of the configurations used in (1). Theoretical intensity calculations[13] show that the $N \rightarrow E_1$ transition is of the forbidden type while

$N \rightarrow E_2$ must have a very low intensity. Both of these transitions can obtain some intensity from electronic-vibrational coupling[15] but at best are expected to be weak. In contrast with these low intensities, that predicted for the $N \rightarrow X$ transition is very large.[16] On the basis of these predicted intensities it is logical to assign the weak region which apparently comes around $\lambda 2000$ to the $N \rightarrow E_1$ transition and the strong region following this to the $N \rightarrow X$ transition. The weak $N \rightarrow E_2$ transition must lie underneath the $N \rightarrow X$ region or may come at still shorter wave-lengths.

The positions observed for the $N \rightarrow X$ and the $N \rightarrow E_1$ absorptions in the COO^- ion relative to the corresponding weak absorption at $\lambda 2900$ in aldehydes and ketones can, in part, be explained by the fact that the oxygen atom in aldehydes and ketones has more negative charge than either of the oxygen atoms in the ion. The excited MO may also have a somewhat higher energy in the ion than in the aldehydes and ketones. These facts will be discussed further in a later paragraph.

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[12] There is evidence for believing φ_1 and φ_2, and also ψ_1 and ψ_2, are nearly degenerate (reference 10, footnote 11). This means that localized MO's are appropriate for describing the O_1-C and O_3-C σ bonds. Since interaction between these localized MO's must be small, the semi-localized MO's φ_1 and φ_2 can be approximated by respectively taking positive and negative linear combinations of the localized bonding MO's of the O_1-C and O_3-C bonds. Similarly ψ_1 and ψ_2 can be approximated by taking corresponding combinations of the two antibonding MO's.

[13] These calculations were made in the same way as in reference 4.

[14] The simplest possible LCAO approximations for ω_1 and ω_2 can be written as $(q_1+q_2)/2^{\frac{1}{2}}$ and $(q_1-q_2)/2^{\frac{1}{2}}$, respectively. Better approximations would require the presence of some $2p_z$ and $2s$ of carbon in ω_1 and some $2p_y$ of carbon in ω_2.

[15] G. Herzberg and E. Teller, Zeits. f. physik. Chemie B21, 410 (1933); H. Sponer and E. Teller, Rev. Mod. Phys. 13, 75 (1941).

[16] The calculated value of Q^2 (dipole moment integral) for the $N \rightarrow X$ transition is about $0.7A^2$, that for the $N \rightarrow E_2$ transition about $0.002A^2$.

B. Electron Configurations for the COOR Radical

For discussing the electronic structure of the COOR radical, localized MO's can best be used. The R group will be regarded as attached to the O_3 atom by an MO of the σ type. In the acids, strong hydrogen bonding between the H and O_1 atoms will hold the hydrogen in the OCO plane.[17] In the esters the $R-O_3$ bonding MO may possibly have its axis out of the OCO plane. Configurations for the two cases where this axis lies respectively in and perpendicular to the OCO plane will be discussed. The AO of the R group used in describing the $R-O_3$ bond will always be denoted by σ_R. It behaves like $1s$ of hydrogen or $2p\sigma$ of carbon when R denotes an H atom or an alkyl group, respectively.

In place of the φ_1, φ_2, ψ_1, and ψ_2 MO's of the COO^- ion, four localized MO's of the σ type are now used. Two of these, one bonding and one antibonding, are localized in the O_3-C bond, while a similar pair is localized in the O_1-C bond. The carbon AO's appearing in the LCAO MO expressions for these σ MO's are again linear combinations of $2p_z$, $2p_y$, and $2s$ AO's. The carbon AO's directed toward atoms 1 and 3, respectively, will be denoted by $\sigma_{1,2}$ and $\sigma_{3,2}$. The oxygen AO's with which these combine are denoted by σ_1 and σ_3, respectively.

The MO's localized in the $O_1=C$ part of the radical are very much like their respective counterparts in the carbonyl group.[4] They will be described in essentially the same way as in reference 4 except that now two of the O_1 AO's are denoted by q_1 and σ_1 instead of y_0 and z_0, respectively.

Finally, the O_3 atom contains two nearly nonbonding $2p$ electrons with the axes of their wave function perpendicular to both the O_3-C and $R-O_3$ lines.

Wherever possible the letters used below to designate the configurations of the COOR radical have been chosen so that a given state bears the same designation as the state in (1) to which it shows the closest correspondence.

For the case where the $R-O_3$ bonding MO lies in the OCO plane these configurations may be written as follows:

[17] See L. Pauling, reference 9, p. 286.

$$N\text{—}(q_3\sigma_R)^2(\sigma_3\sigma_{3,2})^2(\sigma_1\sigma_{1,2})^2(x_1x_2)^2(x_3)^2(q_1)^2.$$
$$E_1\text{—}(q_3\sigma_R)^2(\sigma_3\sigma_{3,2})^2(\sigma_1\sigma_{1,2})^2(x_1x_2)^2(x_3)^2(q_1)(x_1\bar{x}_2).$$
$$X\text{—}(q_3\sigma_R)^2(\sigma_3\sigma_{3,2})^2(\sigma_1\sigma_{1,2})^2(x_1x_2)^2(x_3)(q_1)^2(x_1\bar{x}_2).$$

$$(2)$$

Analogous configurations for the case where the $R-O_3$ line is perpendicular to the OCO plane may be written as follows:

$$N\text{—}(x_3\sigma_R)^2(\sigma_3\sigma_{3,2})^2(\sigma_1\sigma_{1,2})^2(x_1x_2)^2(q_3)^2(q_1)^2.$$
$$E_1\text{—}(x_3\sigma_R)^2(\sigma_3\sigma_{3,2})^2(\sigma_1\sigma_{1,2})^2(x_1x_2)^2(q_3)^2(q_1)(x_1\bar{x}_2).$$
$$E_2\text{—}(x_3\sigma_R)^2(\sigma_3\sigma_{3,2})^2(\sigma_1\sigma_{1,2})^2(x_1x_2)^2(q_3)(q_1)^2(x_1\bar{x}_2).$$

$$(3)$$

Here, as in the previous article,[4] any symbol such as x_1x_2 indicates an MO formed as a linear combination of the two AO's indicated. The bars denote antibonding MO's.

In both of these configurations the lowest excited MO is of the x type and is exactly analogous to the lowest excited MO of the carbonyl group. The non-bonding electrons on the O_1 atom are assumed to have a higher energy than those on the O_3 atom. This is not certain—particularly in the acids where the O_3 atom is able to draw charge from the hydrogen atom. However, this order proves to be unimportant for the interpretation of the spectrum at longest wave-lengths. Similarly the order for the energies of the bonding σ MO's is uncertain. These MO's are not involved in any of the transitions considered here and their energy order does not need to be known.

The configurations given in (2) and (3) are equally capable of explaining the observed absorption of the COOR group. Intensity calculations again show that the longest wave-length absorption should be weak, in agreement with what is observed for the region at $\lambda 2100$ in all acids and esters. An interesting fact is that the $N \rightarrow X$ transition in (2) is found to have an intensity which depends strongly on the amount of interaction between the x_3 AO and the x_1x_2 and $x_1\bar{x}_2$ MO's. Although the $N \rightarrow X$ intensity must be very strong in the ion where this interaction is at its strongest, it may be weak in the COOR group.

The region at $\lambda 1700$ in acids and esters can possibly be explained by the $N \rightarrow X$ transition. However, the spectra of aldehyde and ketones show that an absorption characteristic of the $>C=O$ group also occurs in this region. It is
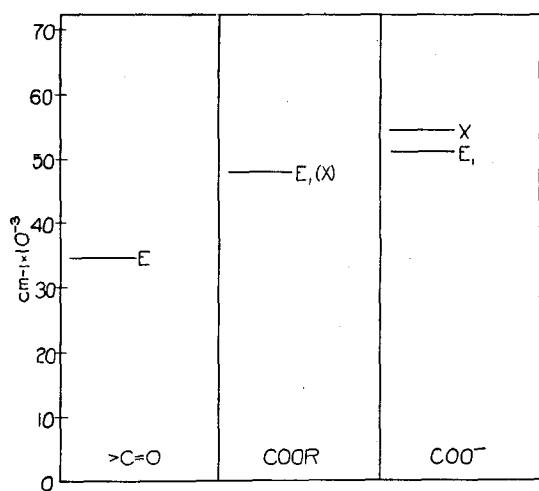
FIG. 3. Energies for the low excited states in $>C=O$, COOR, and COO$^-$ relative to their normal states. The notation for the states is the same as that used in configurations (1), (2), (3) and in reference 4. The energies for the lowest states have been determined from the longest wave-length absorptions which come, respectively, at $\lambda 3000$, $\lambda 2100$, and probably just below $\lambda 2100$ in $>C=O$, COOR, and COO$^-$. The X state in COOR is placed in parenthesis because it very probably may be higher than the E_1 state. The absorption below $\lambda 1900$ in COO$^-$ is here ascribed to the $N \rightarrow X$ transition. The frequency of its maximum is uncertain but is higher than for the $N \rightarrow E_1$ absorption.

possible that in COOR one or more transitions involving excitation of the non-bonding electrons to MO's of the σ type which are $C-O$ or O_3-R antibonding may well produce this absorption. While these transitions appear to include those most likely to produce the $\lambda 1700$ absorption, other possibilities exist and an unambiguous assignment does not seem possible at present.

III. COMPARISON OF THE LONGEST WAVE-LENGTH ABSORPTIONS IN $>C=O$, COOR, AND COO$^-$

In the normal state of the carbonyl group the carbon is positively, and the oxygen negatively, charged. The presence of the extra oxygen atom (O_3) in the COOR group must cause still more negative charge to leave the carbon. The total charge lost by the carbon is then divided between two oxygen atoms each of which probably has less negative charge than that held by the oxygen of the carbonyl group. As a result the non-bonding electrons should have a higher energy in $>C=O$ than in COOR and perhaps COO$^-$. In COOR and COO$^-$ the excited x MO is pushed up by interactions between the x_3 AO

and the $x_1\bar{x}_2$ MO. In COO$^-$ the x_1 and x_3 AO's are equivalent and this interaction is very strong. It is reasonable to assume that the excited x MO has its highest energy in COO$^-$ and probably its lowest energy in the carbonyl group. These facts show that, if the mechanisms proposed in Part II to explain the longest wave-length absorptions are correct, the absorptions should occur at progressively shorter wave-lengths on going from $>C=O$ to COOR and COO$^-$. This is observed to be the case, the absorptions coming respectively near $\lambda 2900$, $\lambda 2100$, and below $\lambda 2000$.

In COOR the weak absorption is somewhat stronger than in the carbonyl group. It is possible that the $N \rightarrow X$ absorption, although weak, contributes to this absorption. However, the absorption region next following is about 10,000 cm^{-1} away in COOR and about 15,000 cm^{-1} away in the carbonyl group. The weak absorptions may well steal intensity[15] from these adjacent regions and the situation for doing this is more favorable in COOR.

IV. POSITION OF THE R GROUP IN ESTERS

Theoretically it might be possible to compare the positions and intensities for the absorptions in the acids and esters and thereby determine whether the $O-R$ line in esters had any definite orientation with respect to the OCO plane. However, the data thus far available are not sufficient for this purpose. The broad aspects observed for the longest wave-length absorptions are equally explicable using either configuration (2) or (3). A much more detailed knowledge of the positions and intensities of the absorptions throughout the vacuum regions seems necessary if progress is to be made in this direction.[18]

V. SUMMARY

The evidence presented above makes it appear quite certain that the relatively weak absorption at $\lambda 2100$ in the COOR group is produced by a transition to the E_1 state in (2) or possibly, in esters, to states somewhat like E_1 and E_2 of (3).

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[18] Studies of the infra-red absorptions of esters to determine a possible orientation of the $O-R$ line apparently have not been made. Any tendency toward bonding between the R group and the O_1 atom should affect the $C=O$ vibration. The author is indebted to Mr. R. Schlegel of the University of Illinois for correspondence about this point.

The absorptions at $\lambda1700$ 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 $\lambda1900$ 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.

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-Ansidei[2] 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 investigators[3] 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 Miller[4] 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).