# THE INFRARED AND ULTRAVIOLET SPECTRA OF ACROLEIN

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# Summary

The α,β -unsaturated aldehyde acrolein $CH_2 = CH - CHO$ and its formyl deuterated derivative acrolein - $d_1$ $CH_2 = CH - CDO$ have been synthesised by different methods and their infrared and near ultraviolet spectra recorded. Attempted syntheses of acrolein - $d_3$ $CD_2 = CD - CHO$ have resulted in mixtures of isotopic derivatives. With the aid of mass spectroscopic and nuclear magnetic resonance techniques, the compositions of these mixtures have been estimated thereby revealing, in some measure, the mechanistic interpretation of the reaction involved.

Measurements of both the infrared and near ultraviolet vapour spectra have enabled frequencies to be assigned to all but two of the eighteen fundamental vibrational modes for each of the two molecules.

Two transitions, both of the $\pi^* - \pi$ type, have been identified in the near ultraviolet region. The lowest in energy, a weak triplet system, occurs about 4,061 Å. The other transition, characterised by the vibrational analysis as $A'' - A'$, gives rise to a band system having its origin at 3,867 Å. Six fundamental vibrations of the upper state, two of them non-totally symmetric, have been identified. The torsional vibration frequencies in the upper state reflect changes in bond order which confirm the diradical nature of the excited state, a concept essential to recent interpretations of photochemical rearrangements.

# Preface

I wish to record my appreciation and thanks to Dr. J.C.D. Brand, who supervised the work herein described, for his constant guidance and interest. It is also a pleasure to express my thanks to Mrs. F. Lawrie and Miss M. Mackay for technical assistance. Finally, I am indebted to the Department of Scientific and Industrial Research for financial support in the form of a Research Studentship.

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# I. THEORETICAL INTRODUCTION

The integrity of a molecule is uniquely dependant on the electrons contributed by the atoms which that molecule comprises. Ultraviolet spectroscopy, as outlined in this section, affords a direct means of enquiry into many aspects of the behaviour of these electrons in their molecular environment and is thus a field of study of fundamental importance to chemistry as a whole.

## I. 1. Electronic States

In forming a molecule, the electronic orbitals of the constituent atoms combine in specific ways, determined by their number and type, to produce a series of molecular orbitals, each with a characteristic energy. Naturally the set of molecular orbitals of lowest energy, which are consistent with the interatomic combination rules, will be those operative in the normal, stable molecule. This self consistent system of orbitals is then said to constitute an electronic state of the molecule, the lowest in energy, the ground state, corresponding to the stable molecule under normal circumstances. A number of states of higher energy may exist and under suitable conditions it will be possible for the molecule to exist in, or at least undergo transitions to, these states. This series of electronic states is indeed analogous to the electronic levels of discrete atoms.

In the case of diatomic molecules, the summation of the Coulomb potential ofthe nuclei and the electronic energy, i.e. the combination of the internuclear repulsion and the bonding properties of the electronic orbitals, can be represented by a series of two-dimensional potential curves in which energy is plotted against internuclear distance. Each electronic state resulting from these summations or combinations then appears as a discrete curve which corresponds to a stable molecule only if there is a turning point of minimum energy. In fig. 1 a series of such curves is shown for the lithium $Li_2$ molecule with the particular combining orbitals of the lithium atoms shown for each state.

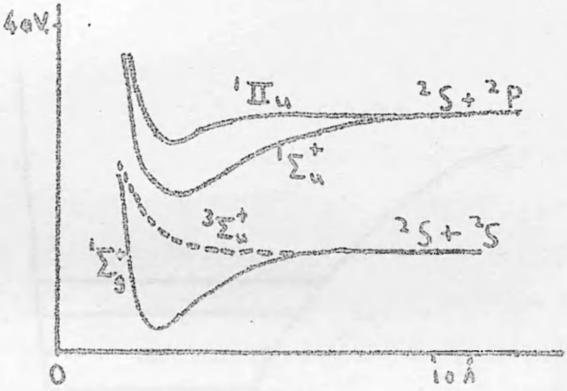


Fig. 1.

Of the four curves, only that labelled $^3\Sigma_u^+$ represents an unstablemolecule. When this type of representation is extended to polyatomic molecules, the simple two-dimensional potential curve develops into a multi-dimensional potential surface. In such a molecule of, say N atoms, there are 3N degrees of freedom of which six, five in a linear molecule, refer to translational and rotational motion of the molecule as an entity. The remaining 3N - 6, 3N - 5 in linear molecules, degrees of freedom are attributable to nuclear displacements within the molecule. In fact, these are the fundamental vibrational modes adopted by the atoms in periodic motion about their equilibrium positions. Thus, in a diatomic molecule, there is 3N - 5 = 1 nuclear displacement which is the bond stretching vibration. The energy associated with this nuclear motion is also quantised and can be represented in a potential curve diagram as a series of discrete horizontal lines within the potential minimum 'well'. The points of contact with either side of the potential minimum well then represent the classical turning points of the periodic nuclear displacement. See fig. 2.

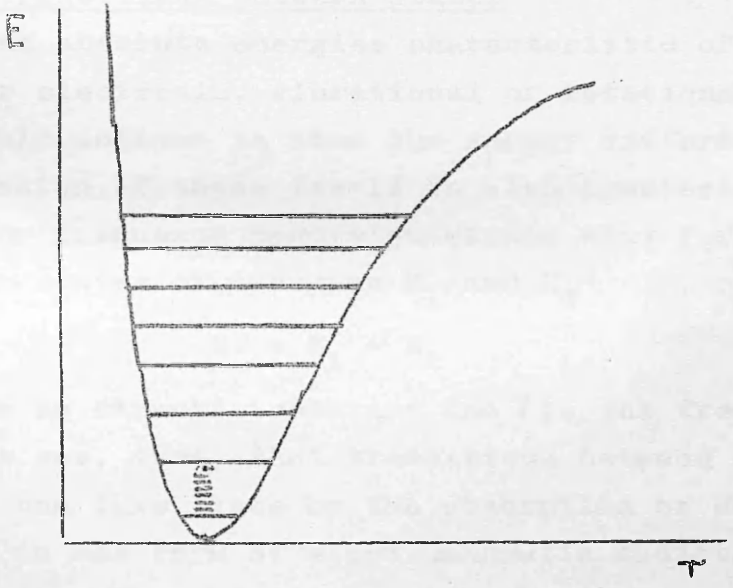


Fig. 2.

In a non-linear triatomic molecule, there are 3N - 6 = 3 nuclear displacements and in consequence a four dimensional potential surface is required to represent the electronic states fully. However it is possible to return to the

Of course in vibrational spectra, transitions will also concern the smaller spaced rotational levels, while in electronic spectra, the whole range of possible energy differences will be apparent. Thus the complexity of spectra increases in the progression from rotational to electronic. On a potential curve diagram, a line drawn vertically from any level, vibrational or rotational, in one electronic state to any level in an adjacent electronic state represents a possible transition which could appear as absorption or emission in the ultraviolet region. The length of the line on the diagram is proportional to the frequency of the observed absorption or emission. It is obvious that in such a diagram as fig. 3(a) an extremely large number of such transitions are possible and there remains, of course, the other diagrams representing other vibrations of the molecule. If all these transitions actually occurred, the ultraviolet spectrum would merely be a meaningless continuum composed of overlapping and superimposed transitions. That the ultraviolet spectra of many polyatomic molecules show discrete, sharp and regular band structures is proof that highly selective restrictions apply and only a small minority of the possible transitions actually take place. So far we have noted no distinguishing features of the energy levels which could form a basis for this selection process. It is obvious that no random mechanism of selection is operative but rather that there exists a highly organised system which confers special characteristics on each energy level according to a definite pattern. At this point we must, therefore, consider afresh the origin of electronic states and decide what other characteristics are inherent in these states in addition to specific energy values.

## I. 3. Selection Rules

(a) The electronic states of an atom are characterised in addition to their energies by the terms S, P, D, F .... where these letters refer to 0, 1, 2, 3 .... units of angular momentum, each unit being defined as $h/2\pi$. In the extension from the atom to the diatomic molecule, the S, P, D, F terms correspond to the $\Sigma$, $\Pi$, $\Delta$, $\Phi$ terms of the molecule and it remains convenient to refer to the classification in terms of angular momentum. However, inspection of the shapes of the S, P, D, F atomic orbitals makes it clear that basically it is their symmetry types that give rise to the typical angular momentum values. Classification with reference to the symmetry rather than the angular momentum of the electronic orbitals has wider applications and is more realistic. A polyatomic molecule no longer possesses the spherically or cylindrically symmetric potential fields of the atom and diatomic molecule, but it may posses certain characteristic symmetry operations with regard to which the potential field is still symmetric and it is by these operations, which together form a self-consistent set, that the electronic state of the molecule is characterised. Each molecule belongs, by reason of the symmetry elements present in its particular geometry, to one of the algebraic point groups. Many molecules possess only the trivial identity operation and thus belong to the group C, in the Schoenflies notation. A highly symmetrical molecule, such as benzene, will belong to a higher group, in this case $D_{6h}$. All homonuclear diatomic molecules belong to group $D_{\infty h}$.

The effect of a symmetry operation of a group on the electronic wavefunction may be characterised by a positive or negative number. For example, if a wavefunction changes sign on reflection in a mirror plane, then the character of the reflection operation is in this instance -1 whereas if the wavefunction remains unchanged by the operation the character is +1. In this way a set of numbers, not necessarily integers, each member of the set corresponding to a symmetry operation of the point group of the molecule, is obtained for a particular electronic wavefunction. These numbers are then found to multiply in such a way as to obey the fundamental rules of algebraic group theory. Together the set of characters is then said to constitute a 'representation' of the group. A different wavefunction arising from another electronic state of the molecule might give a different set of characters forming another representation of the same group. Although it may appear that the typical characters of a group could occur together to form a large number of representations, it must be remembered that the symmetry operations are not independent of each other and, therefore, only a small number of the representations are distinct and independent of each other. These independent or 'irreducible' representations, of which there are a characteristic number for each point group, are normally called 'symmetry species' in molecular spectroscopy. We see then that each electronic state and its wavefunction are characterised by their symmetry species. Referring again to fig. 1, the lowest state of the lithium molecule is totally symmetric while the next two higher states are asymmetric to inversion through the centre of symmetry and to rotation about the two-fold axis perpendicular to the infinity-fold axis along the bond. The various point groups and the details, conventions and symbols associated with them have been comprehensively recorded in a number of treatises on the subject.[1-3]

Symmetry considerations are not limited to the electronic wavefunctions and orbitals. As we have already seen, a molecule of N atoms possesses 3N degrees of freedom and each of these can be transformed in some characteristic way by a specific symmetry operation of the molecular point group. Again, the characters of these transformations combine in specific ways giving rise to representations or symmetry species.

Thus the 3N - 6 vibration modes, the rotation of the molecule about the three principal axes and the related wavefunctions all have particular symmetry properties. Symmetry species can also be assigned to the translational displacements along the three molecular axes. Each of the 3N degrees of freedom can then be characterised by one of the symmetry species of the molecular point group.

The radiation normally concerned in molecular electronic spectra arises from the oscillation of an electric dipole. Although magnetic dipole transitions almost certainly occur, they are usually extremely weak and we shall not deal with them further. The electric dipole has an associated dipole moment with components along the x, y, z molecular axes. These components then have the symmetry properties of translations along the respective axes.

(b) The electronic transition probability is given by the expression

$$\int \psi_e' M \psi_e''^* d\tau_e \qquad (1)$$

where $\psi_e'$ and $\psi_e''$ are the electronic wavefunctions for the upper and lower states respectively, the asterisk denoting the complex conjugate value. M is the dipole transition moment and $d\tau_e$ indicates that the integration is carried out over all the electron configurations.

The effect of a symmetry operation on the integration is merely to change the order of the process and so should not alter the final value. If, however, due to the symmetry properties of the integrand, the operation changes the sign of the integrand, then two inconsistent conditions exist. In these circumstances, the only possible value of the integrand is zero. Thus, if the product of the symmetries of $\psi_e'$, $\psi_e''^*$ and M is a non-totally symmetric term, the transition probability will be zero and the transition is said to be 'forbidden'.

For an allowed transition, the product of the symmetry species of $\psi_e'$ and $\psi_e''$ must yield a term identical to that of one of the x, y, z - components of M since only two such identical species will multiply to yield the required totally symmetric species of the integrand.

We see then that transitions can only take place between electronic energy levels having symmetry species which yield a product identical to one of the three components of translational motion. As an example, we give the species table for group $D_{2h}$ and also the table of direct products. (Tables 1 and 2).

Table 1

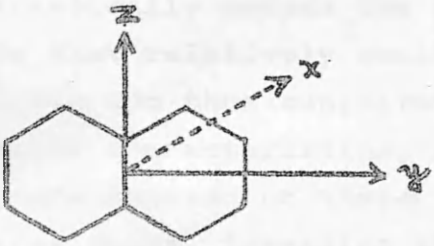
| $D_{2h} = V_h$ | E | $C_2(z)$ | $C_2(y)$ | $C_2(x)$ | i | $\sigma(xy)$ | $\sigma(zx)$ | $\sigma(yz)$ | |
|---|---|---|---|---|---|---|---|---|---|
| $A_g$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| $B_{1g}$ | 1 | 1 | -1 | -1 | 1 | 1 | -1 | -1 | $R_z$ |
| $B_{2g}$ | 1 | -1 | 1 | -1 | 1 | -1 | 1 | -1 | $R_y$ |
| $B_{3g}$ | 1 | -1 | -1 | 1 | 1 | -1 | -1 | 1 | $R_x$ |
| $A_u$ | 1 | 1 | 1 | 1 | -1 | -1 | -1 | -1 | |
| $B_{1u}$ | 1 | 1 | -1 | -1 | -1 | -1 | 1 | 1 | $T_z$ |
| $B_{2u}$ | 1 | -1 | 1 | -1 | -1 | 1 | -1 | 1 | $T_y$ |
| $B_{3u}$ | 1 | -1 | -1 | 1 | -1 | 1 | 1 | -1 | $T_x$ |

Table 2

| | $A_g$ | $B_{1g}$ | $B_{2g}$ | $B_{3g}$ | $A_u$ | $B_{1u}$ | $B_{2u}$ | $B_{3u}$ |
|---|---|---|---|---|---|---|---|---|
| $A_g$ | $A_g$ | $B_{1g}$ | $B_{2g}$ | $B_{3g}$ | $A_u$ | $\underline{B_{1u}}$ | $\underline{B_{2u}}$ | $\underline{B_{3u}}$ |
| $B_{1g}$ | | $A_g$ | $B_{3g}$ | $B_{2g}$ | $\underline{B_{1u}}$ | $A_u$ | $\underline{B_{3u}}$ | $\underline{B_{2u}}$ |
| $B_{2g}$ | | | $A_g$ | $B_{1g}$ | $\underline{B_{2u}}$ | $\underline{B_{3u}}$ | $A_u$ | $\underline{B_{1u}}$ |
| $B_{3g}$ | | | | $A_g$ | $\underline{B_{3u}}$ | $\underline{B_{2u}}$ | $\underline{B_{1u}}$ | $A_u$ |
| $A_u$ | | | | | $A_g$ | $B_{1g}$ | $B_{2g}$ | $B_{3g}$ |
| $B_{1u}$ | | | | | | $A_g$ | $B_{3g}$ | $B_{2g}$ |
| $B_{2u}$ | | | | | | | $A_g$ | $B_{1g}$ |
| $B_{3u}$ | | | | | | | | $A_g$ |

From table 1 it can be seen that $B_{1u}$, $B_{2u}$, $B_{3u}$ are the species of translational motion along the z, y, x axes respectively. Most ultraviolet spectra arise, in normal circumstances, from transitions from or to the ground state which is totally symmetric ($A_g$) and thus the allowed transitions for the group $D_{2h}$ are $B_{1u} - A_g$, $B_{2u} - A_g$ and $B_{3u} - A_g$. The direction of polarisation is different in each case and consequently, if this direction is known, the electronic upper state species can be uniquely determined. There are two distinct methods of determining the direction of a transition and both will be described in a later section. (I. 6(d)).

The application of these principles is well illustrated by the recent work of Craig et al.[4] and McClure[5] on the 3,200Å system of naphthalene which has $D_{2h}$ symmetry. The symmetry axes are set up as shown below in the orientation recommended by the Joint Commission for Spectroscopy [6].



The pure electronic transition has been shown by two independent methods to be polarised along the y-axis and by inspection of tables 1 and 2 it can be seen from this information that the transition is $B_{2u} - A_g$.

(c) At this point another type of restriction on transitions must be considered. This concerns the resultant electron spin of each state, normally expressed as the electron multiplicity 2S+1 where S is the resultant spin of the electrons, each of which has $S = \pm\frac{1}{2}$. Configurations with no unpaired electrons have S = 0 and a multiplicity of one. Those with one unpaired electron have $S = \frac{1}{2}$ and a multiplicity of two. These are called singlet and doublet states and correspond in most cases to the stable ground states of a molecule and its ion. Triplet states, of course, have two unpaired electrons. If the multiplicities of the combining electronic states are different, it is found that the integral (I. 3b (1)) vanishes so that only singlet-singlet, doublet-doublet and similar transitions are allowed, while singlet-triplet transitions are forbidden.

(d) Another type of selection rule makes forbidden transitions which excite more than one electron.

We now have a set of selection rules belonging to three distinct types which determine whether transitions between various energy levels are allowed or forbidden.

These rules, when applied to the vast number of possible combinations of energy levels, electronic and otherwise, of a molecule, drastically reduce the potential number of transitions to that relatively small number which are actually observed and thus constitute a molecular spectrum. Moreover, special characteristics, such as direction of polarisation, are imposed on these 'active' transitions by the selection rules, investing them with criteria additional to frequency by which they may be distinguished and assigned.

(e) Before we consider some of the more important ways in which deviations from these selection rules can occur, there is one other major factor governing intensities in electronic transitions.

It was first realised by Franck [7] that electronic transitions take place very much more rapidly than nuclear displacements. It therefore follows that nuclei occupy virtually identical positions before and after the occurrence of the electronic transition. This corresponds in the familiar potential curve diagram to the convention of representing transitions by strictly perpendicular lines between the combining levels. Any deviation from the vertical would imply nuclear motion during the transition. This idea and its quantum - mechanical development by Condon [8] are known as the Franck-Condon principle.

Classical mechanics predicts that the most probable position of the vibrating nuclei is at the turning points of the periodic motion. This prediction is invalidated by quantum - mechanical considerations principally in the case of the zero vibrational levels in which the most probable position is the centre point of the vibration. In moving up the vibrational stack of levels, the classical situation is quickly restored. Consider Fig. 3a which represents two very similar electronic states. The mid-points of the zero levels in each state can be joined by a vertical line which then represents a possible transition.

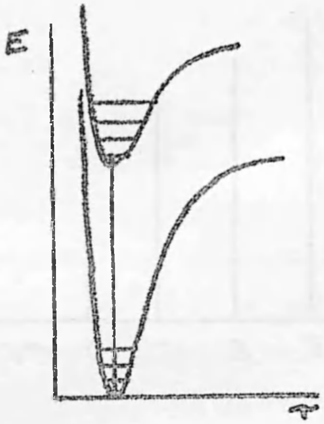


Fig. 3a.

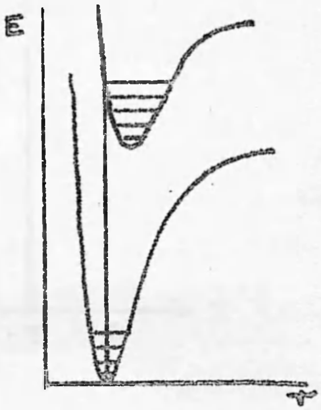


Fig. 3b.

However, in figure 3b, the two states are not at all similar implying a difference in bonding and hence in molecular parameters. A vertical line from the zero level of the lower state cannot pass through the corresponding mid-point of the upper state zero level but must terminate at the turning point of an appropriate excited vibrational quantum. Thus, according to Franck's theory, the absorption spectrum will show no band corresponding to the pure electronic transition, the origin of the spectrum corresponding rather to the electronic jump, plus, in this case, four quanta of the upper state vibration frequency. In fact, as Condon showed, a progression in this vibrational frequency is observed, the intensity increasing in the series v = o, 1, 2, 3, 4 and declining after the maximum at four quanta. (See fig. 3c).

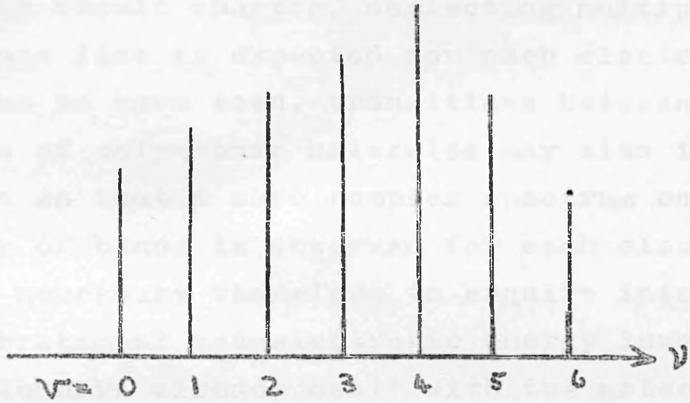


Fig. 3c.

In the first case, where the states are similar and no change in geometry occurs, no marked progression is apparent and the system origin representing the pure electronic jump is the strongest in the spectrum. It should be remembered that this discussion is based on potential curves which are sections of the potential surface representing the complete wavefunctions of the two states and this section corresponds with one of the 3N-6 vibrational modes. This mode in the lower electronic state will be just that which allows the nuclei to approximate in their displacements to the new equilibrium positions appropriate to the upper electronic state.

The Franck-Condon principle then enables estimates of the molecular structure of electronically excited states to be made from the vibrational structure of the spectrum. The particular mode of vibration which forms long progressions indicates the nature of the change in molecular structure while the distribution of intensity over the members of the progression indicates the extent of the change.

## I. 4. The Vibrational Structure of Electronic Spectra

(a) In atomic spectra, neglecting multiplet structure, only one line is expected for each electronic transition but, as we have seen, transitions between electronic states of polyatomic molecules may also involve vibrational quanta so that a more complex spectrum comprising a large number of bands is observed for each electronic transition. It is necessary therefore to enquire into the combination of vibrational and electronic energy levels.

We have already dealt with the molecular electronic wavefunctions and have seen how the symmetry selection rules arise from the characteristic symmetry species of these wavefunctions. Electronic energy, however, does not constitute the total energy of the molecule and discussion of the electronic wavefunction independently therefore implies a factorisation of the total molecular wavefunction into electronic, vibrational, rotational and translational components:

$$\Psi_{total} = \psi_e . \psi_v . \psi_r . \psi_t \tag{1}$$

so that the integral expressing the transition probability is more accurately written:

$$\int \Psi''^{*} M \Psi' d\tau \tag{2}$$

As we now propose to consider the vibrational structure of transitions it is necessary to employ a better approximation to (2) than in previous sections. In place of the pure electronic wavefunction $\psi_e$ we shall adopt the partially factorised 'vibronic' wavefunction $\psi_{ev} = \psi_e . \psi_v$ . In this case the transition probability is given by the integral

$$\iint \psi_e''^{*} . \psi_v''^{*} M \psi_e' . \psi_v' \, d\tau_e . d\tau_v \tag{3}$$

which on factorisation yields

$$\left\{\int \psi_e''^{*} M \psi_e' d\tau_e\right\}\left\{\int \psi_v''^{*} \psi_v d\tau_v\right\} + \left\{\int \psi_e''^{*} \psi_e' d\tau_e\right\}\left\{\int \psi_v''^{*} M \psi_v' d\tau_v\right\} \tag{4}$$

Now, since $\psi_{ev}$, $\psi_e$ , $\psi_v$ are all eigenfunctions of the appropriate Hamiltonian operators, they will be both orthogonal and normalised, i.e. orthonormal.

For transitions between different electronic states the integral:

$$\int \psi_e''^{*} \psi_e' \, d\tau_e = 0 \qquad (5)$$

by the orthogonality condition. Since different electronic states are involved, different operators will apply to the vibrational eigenfunctions and the orthonormal condition will not be maintained. Therefore (4) reduces to:

$$\left\{\int \psi_e''^{*} M \psi_e' \, d\tau_e\right\}\left\{\int \psi_v''^{*} \psi_v' \, d\tau_v\right\} \qquad (6)$$

The first factor in the expression (6) has already been discussed (I. 3 (b)) and we shall now consider the other factor, the Condon Integral, which relates to the vibrational structure of the electronic transition. This integral is non-zero only when the product of the symmetry species of the vibrational wavefunctions contains a totally symmetric term. Since $\psi_v''$ normally refers to the vibrationless ground state, which is always totally-symmetric, it follows that for allowed transitions the species of the vibrational excited state $\psi_v'$ must also be totally symmetric. Thus totally symmetric vibrational fundamentals are unrestricted as to quantum changes in their occurrence in the spectrum and may form regular progressions.

The first excited level of a non-totally symmetric vibrational fundamental is characterised by the symmetry species of that fundamental. The second quantum level is totally symmetric and the third again has the species of the fundamental. In general, even numbered quanta are totally symmetric while odd-numbered quanta have the symmetry species of the fundamental. It follows from this alternation of symmetries that 0 - 0, 0 - 2, 0 - 4 .... transitions are allowed, while 0 - 1, 0 - 3, .... transitions are forbidden. The sequences 0 - 0, 1 - 1, 2 - 2 .... will also be allowed since the product of two identical species yields a totally symmetrical term. Indeed this is apparent from the Franck-Condon Principle since in a potential diagram for a non-totally symmetric vibration the potential curves representing the upper and lower states will have their minima on the same perpendicular line corresponding to fig. 3a. Any other position would imply a change in normal co-ordinates, that is in the upper state geometry. Thus the 0 - 0 band will be the most intense followed by the sequences 1 - 1, 2 - 2 .... It can be seen from this that a progression in double quanta, 0 - 2, 0 - 4 .... would only be developed if the minimum of the upper state curve was displaced thus indicating a change in molecular geometry on excitation. As we have already noted in the previous section, the nature of the change will be indicated by the particular vibration forming the progression.

(b) Inversion Doubling

All non-planar molecules can exist in two identical equilibrium positions which are related by inversion at the centre of mass. Corresponding to each of these positions, there is a potential minimum, the two minima being separated by a barrier, the height of which represents the energy required for the inversion process. Mutual perturbation of the vibrational energy levels in each of the potential wells occurs by reason of the quantum mechanical tunnel effect. This results in a splitting of the energy levels, the magnitude of which increases as the vibrational quantum number 'v' increases and the top of the barrier is approached. In the limit, for levels well above the top of the barrier, the separation of the levels is constant and equal to half that of successive unperturbed levels. Thus the lower levels v = 0, 1 may have undetectably small splittings especially if the energy barrier is substantial.

Another result of this phenomenon is that the members of each pair of levels produced by the splitting are alternately symmetric and asymmetric with respect to reflection in the plane corresponding to the energy maximum of the inversion. In this way, the levels of the whole vibrational stack are alternately symmetric and asymetric to the plane.

These considerations have proved valuable in determining the excited state structures of several molecules (see for example II. 2(a)).

A related type of phenomenon is that of torsional oscillation. The physical basis of this is the rotation of one part or group of atoms of a molecule relative to some other group which constitutes the rest of the molecule in the simplest case. If the two groups between which relative rotation is taking place are identical, a number of identical potential minima characteristic of the group will be found for one complete revolution of 360°. The potential curve is then a periodic function and can be represented by a Fourier series. As in the case of inversion doubling, perturbation of the vibrational levels will occur resulting in splitting characteristic of the number of minima in one revolution. Similarly, if the potential barrier is relatively high, the splitting of the lower levels will be negligible. Fig. 4 represents a curve appropriate to torsion between two $CH_3$ groups.

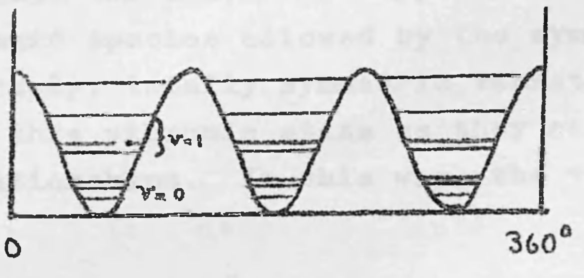


Fig.4

## I.5 Deviations from the Selection Rules

(a) Symmetry Selection Rules. A number of spectra have been attributed to symmetry forbidden transitions, perhaps the most notable example being the ${}^1B_{2u} - {}^1A_{1g}$ transition of benzene. The factorisation of the complete molecular wavefunction into separate electronic, vibrational and rotational components results in a convenient simplification of the theoretical aspects of chemistry but is, nevertheless, an artificial process. In the case of spectra due to symmetry-forbidden transitions, this factorisation is no longer completely valid since there is interaction of the electronic and vibrational wavefunctions. As a result of this interaction the expression (3) in section I. 4(a) cannot be factorised to give (4) and consequently it is the double integral (3),

$$\iint \psi_e''^* \psi_v''^* M \psi_e' \psi_v' \, d\tau_e . d\tau_v$$

rather than (6) which expresses the transition probability. The symmetry species of this 'vibronic' upper state $\psi_e' . \psi_v'$ is then the direct product of the species of the particular vibrational mode and that of the electronic state. If the vibration is totally symmetric, then the symmetries of the vibronic and electronic states will be identical and this is the case in the ground state $\psi_e'' . \psi_v''$. Conversely, a non-totally symmetric vibration may produce a vibronic state different in symmetry from the electronic state. In electronically forbidden transitions there will be some non-totally symmetric vibrational species which, by combination with the electronic upper state species, will yield a vibronic species allowed by the symmetry selection rules. Obviously, totally symmetric vibrations can then combine with this vibronic state as they cannot affect the symmetry relationships. In this way, the vibronic energy level acts as a false origin of the spectrum. The true electronic origin, of course, does not appear. The false origin will be separated to the high frequency side of the electronic origin by the upper state frequency of the vibration which makes the spectrum vibronically allowed.

The interaction of electronic and vibrational states is significant in another way but only for molecules capable of existing in degenerate states. In this instance, the angular momentum of the electronic state and certain vibrational fundamentals may couple to produce complex splitting of the vibrational energy levels. For linear and non-linear molecules this splitting is known as the Renner and Jahn - Teller effects respectively.

The $^1B_{2u} - {}^1A_{1g}$ transition in benzene is forbidden since the species $B_{2u}$ is not appropriate to a translation of the molecule along the x, y or z co-ordinates. However, two degenerate vibrations of $e_{2g}$ symmetry give rise to two progressions each with the interval of the totally symmetric ring breathing frequency since $e_{2g} \times B_{2u} = E_{1u}$ which is the species of translation along either of two perpendicular axes in the plane of the ring. The transition then, is actually the vibronically allowed $^1E_{1u} - {}^1A_{1g}$ although the upper electronic state is $^1B_{2u}$. As expected, the origin is not observed.

The pure electronic upper state of the 3,200Å transition of naphthalene is $B_{2u}$ and consequently is allowed. (See table 1). Two much stronger bands appear to higher frequencies of the electronic origin, which is observed, though weak in intensity, and these can be shown to be polarised differently from the origin. Since the stronger bands are separated from the origin by the frequencies of two $b_{3g}$ vibrations, it is obvious that they represent vibronically allowed transitions in the z direction, the products with the electronic state species being

$b_{3g} \times B_{2u} = B_{1u}$. (See table 2). The spectrum is composed of progressions of totally symmetric vibrations building up on the electonic origin and the two false origins. The direction of polarisation is different for the two band systems. Thus the 3,200Å transition of naphthalene exhibits characteristics of both electronically and vibronically allowed components.

(b) Multiplicity Selection Rule.

Since electronic states comprise small components of multiplet configurations other than the predominant one, this selection rule frequently results in very weak rather than completely absent transitions. This is particularly true of molecules containing heavy atoms. The intensity of such transitions is considerably increased by the presence of paramagnetic impurities.

The 3,400Å singlet-triplet transition of benzene is not observed even with a path length of 22.5 metres of the liquid when carefully deoxygenated benzene is used, although quite moderate path lengths of the vapour suffice under normal conditions.

## I.6 The Rotational Structure of Electronic and Vibrational Spectra.

(a) In discussing the rotational structure of spectra we shall consider, in the first instance, the simpler case in which transitions take place between successive vibrational quanta of the same electronic state. The rotational constants for the upper and lower states of these transitions which will of course give rise to infrared spectra, can be regarded as constant.

The rotational levels of a molecule are characterised by the angular momentum quantum numbers J and, for symmetric tops, K. J refers to the total angular momentum while K is the quantum number of the component of the total angular momentum along the top axis. The inertial axes are labelled a, b, and c so that the moments of inertia about these axes are in the order $I_a < I_b < I_c$. For a symmetric top either $I_a = I_b$ or $I_b = I_c$ according as the top is oblate or prolate. The top axis in the former is the c-axis while in the latter it is the a-axis. For a planar molecule it can be shown that $I_c = I_b + I_a$ but in practice, due to the non-rigidity of the molecule, there is a small positive inertial defect $\Delta = I_c - I_b - I_a$.

Like other types of energy, the rotational energy levels are also characterised by symmetry and selection rules can be derived by generally similar methods as have been indicated previously. An important difference is the occurrence in the transition probability integral of matrix elements of the direction cosines relating the normal space fixed set of co-ordinates to an internal set directed along the inertial axes.

(b) The following set of selection rules can be obtained for symmetric top molecules.

Transition parallel to top axis $\Delta K = 0$ $\Delta J = \pm 1$ for $K = 0$

$\Delta J = 0, \pm 1$ for $K \neq 0$

Transition perpendicular to top axis $\Delta K = \pm 1$, $\Delta J = 0, \pm 1$.

When the selection rule $\Delta J = 0, \pm 1$ is operative, the observed band has three branches P, Q and R corresponding to $\Delta J = -1$, 0 and +1.

In parallel type transitions ($\Delta K = 0$), for each value of K a sub-band comprising P, Q and R branches is formed. The observed band is then the result of a number of these sub-bands of different K value superimposed on each other. From the known energy levels of all these sub-bands, it is apparent that they coincide almost exactly so that the observed band shows a strong Q branch with weaker R and P branches[9]. Due to the $\Delta J = 0, \pm 1$ relationship of the branches and the identical separation of the energy levels in the upper and lower states, the Q branch occupies a central position with the P and R branches to lower and higher frequencies respectively.

For perpendicular type transitions ($\Delta K = \pm 1$), the sub-bands no longer coincide even approximately so that the Q branches do not form a single high intensity maximum but remain discrete, forming a series of intense peaks superimposed on the overlapping P and R branches[10]. Since the separation of the J levels is small in any case, it frequently happens that the sub-band J structure is not resolved and the only visible rotational structure is then the series of intense Q branches. In the parallel case no such series is formed and the band envelope will appear smooth unless the resolution is great enough to allow the appearance of the J structure.

(c) Asymmetric tops have all three moments of inertia different and K ceases to have exact significance as a quantum number. Bands are classified as types A, B and C depending on the orientation of the transition moment with respect to the a, b, c axes. Consideration of the energy levels for various asymmetric tops shows that type C and type A bands will have respectively strong and weak central maxima while type B bands will have a central minimum. The degree of asymmetry is characterised by the parameter $\kappa = (2B - A - C)/(A-C)$ and in fact the oblate and prolate tops are the limits to the range of values which $\kappa$ may assume. The energy levels of the asymmetric top may then be related to the K - values of the oblate symmetric top ($K_c$) and the prolate symmetric top ($K_a$). This classification gives rise to the selection rules:

Transitions parallel to the a-axis $\Delta K_a$ even $\Delta K_c$ odd
" " " " b-axis " odd " odd
" " " " c-axis " odd " even.

The correlation becomes of considerable interest in the case of slightly asymmetric tops such as acrolein which approximates closely to a prolate symmetric top. It is expected that in this case the selection rules and consequent band structure will approximate to those of a prolate symmetric top with the exception that deviations will occur especially at the band centre due to the small degree of asymmetry. The classification of bands as parallel or perpendicular will, however, still be valid.

(d) It has been assumed in all these considerations that the rotational constants of the upper and lower states are identical and this is true to a first approximation for infrared spectra. However, when transitions take place between the rotational levels of different electronic states, the rotational constants are usually different so that the strict order of increasing frequency of the P, Q and R branches is destroyed and thenearly linear relation of J number to frequency is also lost. This frequently results in the lines of the rotational structure bending back on themselves forming a band head. Thus the observed intensity variation in a branch may be governed by factors additional to the normal Boltzmann factor and it may be impossible to identify the band centre without recourse to detailed analysis of the rotational structure. Such an analysis of a number of bands in the ultraviolet spectrum of a molecule will yield values for the upper state rotational constants and in favourable circumstances the structural parameters of the molecular excited state could then be obtained. In cases where the difference in the inertial constants of the combining states is small it is often possible to make a qualitative estimate of the change, particularly in regard to whether the constants increase or decrease in the excited state. An increase in the rotational constants causes the spacing of the lines of the P-branch to diminish while that of the R-branch increases. Thus the lines tend to converge towards the low frequency end of the band which is then said to degrade to the blue. A decrease in the constants on excitation leads to the opposite effect and the band then degrades to the red. Even when the rotational structure is absent, due to insufficiently high resolution or some other cause, it may still be possible to determine the direction if degradation from the band envelope alone. In these circumstances it is also possible to determine the direction of the transition by inspection of the band envelope, the gross features such as the strong Q branch of a parallel band or the central minimum of a type B band being still visible.

A good example of this use of band envelopes concerns the previously cited 3,200Å transition of naphthalene (I. 5(a)). It was pointed out that the transition consisted of an allowed electronic component $^1B_{2u} - {}^1A_g$ directed along the y or a-axis and a vibronically allowed component $^1B_{1u} - {}^1A_g$ directed along the z or b-axis. Since naphthalene is an asymmetric top, it would therefore be expected that the origin and all other bands of the electronically allowed system would be type A. On the other hand, the 'false' origin and other bands of the vibronically allowed system would be expected to be type B. It is found in fact[4] that the former bands possess a prominent Q branch which is absent in the latter, thereby substantiating the type A and B classification. Thus the directions of the transitions are established and the excited states can then be characterised by a symmetry species. This has been accomplished by examination of the rotational envelope alone, no fine structure being apparent.

The direction of a transition moment can be determined directly be measuring the absorption of plane polarised light by a single crystal of the compound. The crystal is orientated so that the direction of the inertial axes is known. It can then be determined which bands appear when light is directed along each axis. A preliminary diffraction study of the crystal is required, however, in order to determine the number and orientation of molecules in the unit cell. The compound under consideration can also be introduced as an impurity into a known host lattice where it will be found to adopt the geometry of the predominant existing lattice. This is the technique adopted in the case of naphthalene which is examined as an impurity in a durene crystal [5]. Low temperatures are necessary in this type of work to reduce the interaction of crystal forces which, however, cannot be ignored.

## II. THE SPECTRA OF RELATED MOLECULES

Acrolein is the first member of the large class of α, β-unsaturated carbonyl compounds. Many important natural products such as vitamin $D_2$, eucarvone and santonin contain this conjugated system. The molecular rearrangements which result from the irradiation of these compounds with ultraviolet light are often novel and complex [12]. The mechanism of these rearrangements is by no means clear, though it seems certain that molecular excited states are involved. The electronic structure of the excited state of the simplest molecule containing the α, β-unsaturated carbonyl group is obviously of interest in this context.

The discovery that the structure of a molecule could change quite radically on excitation to a higher electronic state was foreshadowed by the theoretical work of Mulliken [13] and Walsh [14]. The first proof of the occurrence of these changes was given by King and Ingold for acetylene [15] and since then evidence has accumulated showing that such changes are not uncommon. Both acetylene and ethylene undergo drastic changes in molecular geometry on excitation while formaldehyde similarly experiences less far reaching, but nevertheless definite, changes. In acrolein two of these chromophores are in conjugation and therefore its configuration in the excited state is of interest in view of the behaviour of the two chromophores when in separate molecules. We shall, at this point, consider the previous related spectroscopic analyses of the separate chromophores and later the examples of the two in conjugation.

## II. 1 Carbon - carbon multiple bonds

### (a) Acetylene

The complete analysis of the near ultraviolet spectrum of acetylene by King and Ingold[15] and independently by Innes[16] demonstrated clearly the trans-bent configuration of the lowest excited state of the molecule. In view of the then novel conclusion, it is interesting to follow some of the steps which led to the rejection of the more obvious linear shape and then to the adoption of the trans-bent structure. In so doing, the general methods used in the analysis of ultraviolet spectra and hence in the determination of excited state structures will be seen applied in the particular context of this molecule.

According to the calculations of Ross[17], the state which most nearly approximates in energy to the observed transition is the $\Sigma_u^+$ state. However, the main bands of the spectrum are found to have P, Q and R branches although, according to the selection rules, transitions to any $\Sigma$ state from the ${}^1\Sigma_g^+$ ground state should give rise to bands with P and R branches only.

Vibrational analysis of the spectrum provides further serious problems. The most important progression and the only one originating from the vibrationless ground state extends over five quanta and must be assigned to a totally symmetric vibration which, since the interval is 1049 cm$^{-1}$, can only be the carbon - carbon stretching vibration. The progression reaches an intensity maximum at the fifth quantum and the Franck-Condon principle makes it necessary to explain this by assuming a large increase in the carbon - carbon bond length, giving an excited state value of 1.6 Å. However, detailed rotational analysis gives a value for the constant B of 1.10 cm$^{-1}$ which corresponds to a carbon - carbon bond length of 1.27 Å.

This vibration shows a marked hydrogen isotope effect, the frequency falling by about 200 $cm^{-1}$ in the dideutero derivative. Since, in a vibration of this type, there is little relative motion of the hydrogen nuclei, the large isotope effect is inexplicable.

The ground state frequency progression in the 600 $cm^{-1}$ vibration gives rise to even more difficulties. This progression extends over five successive quanta and can only be assigned to the $\Pi_g$ trans - bending vibration. Not only is the formation of a long progression in such a non-totally symmetric vibration forbidden by the Franck-Condon principle, but the selection rules also strictly forbid the appearance of odd quantum number bands.

It is obvious that the formulation of the excited state as a linear structure, similar to the ground state, is incorrect, but it still remains to decide precisely in what way and to what extent the excited state structure deviates from linearity.

It is possible to do this by consideration of the rotational structure alone without recourse to evidence based on the vibrational data although this in itself is sufficient to indicate the excited state structure. Thus there are two independent methods, both of which lead to the same conclusion.

The temperature dependent progressionsin the ground state $\Pi_g$ trans-bending frequency are made up of pairs of bands about 600 $cm^{-1}$ apart with a spacing of alternately 60 $cm^{-1}$ or 120 $cm^{-1}$ between the members of each pair. The rotational structure shows that the transition moment is perpendicular to the a-axis so that the selection rule $\Delta K = \pm 1$ must apply. It follows from the assumption of the trans-bent structure that the inertial constant $A'$ is about 10 $cm^{-1}$ while $B'$ and $C'$ remain substantially unchanged at about 1 $cm^{-1}$. The rotational energy levels of the bent upper state are given by the equation:

$$E = \tfrac{1}{2}(B + C)\,J(J + 1) + \left[A - \tfrac{1}{2}(B + C)\right] K^2$$

The progression must originate from one quantum of the $\Pi_g$ vibration above the ground state, i.e. with $K'' = 1$. For transitionsfrom this level to obey the $\Delta K = \pm 1$ rule they must terminate in the $K = 0$ or $K = 2$ upper state levels. These two possibilites explain the occurrence of the pairs of bands. If the approximate values are substituted for A, B and C in the given equation it can be seen that the second of the two terms vanishes for $K = 0$ while for $K = 1$ its value is of the order of 40 $cm^{-1}$. Thus the expected difference in energy between the two possible transitions is around 40 $cm^{-1}$ which is in good agreement with the observed separation within the pairs. The 600 $cm^{-1}$ difference between each pair corresponds, of course, to one quantum of the $\Pi_g$ bending vibration. The larger separation of 120 $cm^{-1}$ results from transitions of higher K. Another piece of evidence in favour of the trans-bent structure can be deduced from the J-structure intensities. Innes showed that for angles between the two CCH planes of 45° - 135° the molecule would very closely approximate to a symmetric top. Now, since there exists a 10% difference between $I_b$ and $I_c$ in the excited state, the value of the interplanar angle must be very close to either 0° giving a planar cis configuration ($C_{2v}$ model) or 180° giving a planar <u>trans</u> configuration ($C_{2h}$ model). The decision between these two possibilities is based on the alternation in the intensities of the lines of the J-structure. This alternation is caused by the different statistical weights of the parallel and opposed spins of the two equivalent hydrogen nuclei. It can be shown by the application of symmetry theory to the permutation of the hydrogen nuclei that when the c-axis of the molecule is coincident with the two-fold axis of symmetry (i.e. the $C_{2h}$ model) the alternation in intensities is such that, for both K = 0 and K = 1 (lower levels), the stronger lines have J numbers either all odd or all even. On the other hand, when the b-axis is coincident with the symmetry axis (i.e. the $C_{2v}$ model), then for K = 0, lines with J odd are stronger while for K = 1 (lower levels) those with J even are stronger or vice versa. Study of the observed intensities makes it clear that the former is the case so that the excited state must adopt the $C_{2h}$ model. That is, it takes on a trans-bent configuration.

Using the same intensity alternation in conjunction with the selection rules for an asymmetric top, it can be shown that the electronic symmetry species of the upper state is $A_u$. This conclusion can be reached more directly. We have just seen that the excited state adopts the $C_{2h}$ symmetry model with the c-axis coincident with the two-fold axis and by inspection of the bands it is obvious that the electronic transition moment is parallel to the c-axis. Consequently the electronic orbitals of the upper state are antisymmetric with respect to reflection through the molecular plane.

The reinterpretation of the vibrational structure of the spectrum on the basis of the trans-bent $A_u$ excited state at once resolves the many inconsistencies and difficulties inherent in the concept of a linear excited state.

The prominent 1050 $cm^{-1}$ progression can now be much more reasonably interpreted as a totally symmetric ($A_g$) trans-bending vibration, which, by the Franck-Condon principle, would be expected to give rise to long progressions in view of the large change in molecular geometry. The assignment of this frequency as a bending vibration immediately overcomes two of the problems encountered by the linear structure. It is no longer necessary to postulate a greatly lengthened carbon - carbon bond and thus the structure suggested by the vibrational analysis becomes fully consistent with the moments of inertia calculated from the rotational analysis. In addition the large isotope effect can now be easily understood since the bending vibration produces relatively large displacements of the hydrogen nuclei.

The difficulties encountered in the lower state frequency progression are also eliminated by the adoption of the bent upper state. The symmetry restrictions on the appearance of odd quanta of the $\Pi$g fundamental disappear and on Franck-Condon grounds it is expected that this vibration will form 'hot' progressions despite the unfavourable Boltzmann Factor, since it is just this type of vibration which displaces the nuclei into the excited state equilibrium positions.

## II. 1 (b) Ethylene

In contrast to acetylene, the spectrum of ethylene is diffuse and consequently the assignments and postulated upper state geometries are much less certain.

In the near ultraviolet, Reid[18] has observed a progression of diffuse bands around 2,600 - 3,480 Å. The interval is about 995 $cm^{-1}$. If this absorption is due to the lowest singlet-triplet transition, it would be predicted that the $CH_2$ groups would be twisted through 90° relative to each other and the 995 $cm^{-1}$ frequency might correspond to the upper state torsional vibration. However, the spectrum is extremely weak requiring path lengths of up to 2.5 metres of liquid ethylene, and it was thought that the absorption might be due to impurities. However Evans[68] has confirmed that the observed bands are in fact due to a triplet transition of ethylene. This was done by observing the increase in band intensities when a paramagnetic substance, actually oxygen, was added to the ethylene. See I.5 (b).

The first well established absorption region of ethylene begins at 2026 Å. A long progression of diffuse bands rises in intensity towards shorter wavelengths and eventually becomes a continuum underlying the strong discrete bands of the Rydberg transition at 1750 Å[19,20]. The absorption is assigned to a $^1B_{1u} - {}^1A_{1g}$ transition analogous to the Schumann-Runge system of oxygen. According to theoretical predictions, the carbon-carbon bond should be considerably lengthened and the planar configuration should correspond to an energy maximum in the upper state.

The origin is not observed and so the vibrational numbering cannot be established directly. By making use of the isotopic shift in frequency for $C_2D_4$ and consideration of the zero point energies, a value for the origin was obtained. Upper state values for the main progression forming frequency, the carbon-carbon double bond stretching vibration, are very low at about 850 $cm^{-1}$ and calculations based on analogy with the similar oxygen case indicate a bond length of 1.69 Å. The increase of 0.34 Å would, by the Franck-Condon principle, explain the weakness and disappearance of the spectrum near the origin. There is insufficient evidence from the torsional frequency, which also appears to be active in the spectrum, to confirm or invalidate the theoretical upper state in which the $CH_2$ groups are twisted through 90° relative to each other. Walsh[21] has suggested that, in addition, the upper state is bent or staggered, the carbon atoms being out of the plane bisecting the HCH angle.

A second transition, in this instance to a Rydberg state, has its origin at 1,744 Å and is characterised by a short progression of pairs of bands. Price and Tutte[19] showed that this transition could be fitted into the Rydberg series defined by the formula

$$\nu_0 = 84{,}750 - \frac{R}{(n + 0{\cdot}91)^2}, \quad n = 2, 3, \cdots 6.$$

The progression is formed by the totally symmetric carbon-carbon stretching vibration and the spacing within the pairs corresponds to two quanta of the non-totally symmetric torsional vibration. Product rule calculations making use of the $C_2D_4$ measurements establish the $\nu_2$ assignment beyond doubt and the low value of the torsional vibration plus the fact that it yields a reasonable value for the cis - trans energy barrier leaves little doubt that this assignment is also correct. However, the isotope ratio calculations give abnormal values and, in addition, treatment of the upper state as a torsional oscillator-rotator reveals that the simple cosine expression:

$$V = \tfrac{1}{2} V_0 ( 1 - \cos 2\theta)$$

is not an adequate description of the potential curve. It appears that the real shape of the barrier is considerably different. On this evidence there is a possibility that the equilibrium configuration is slightly non-planar. For transitions between two planar states, non-totally symmetric vibrations such as $\nu_4$ should be excited with only 0, 2, 4 .... quanta, exactly as observed. The deviation from planarity cannot, therefore, be appreciable. Other Rydberg transitions have been observed but little detailed information is available.

The $A_u - \Sigma_g^+$ transition of acetylene and the ${}^1B_{1u} - {}^1A_{1g}$ transition of ethylene are both $\pi^* - \pi$ in type and correspond to the transfer of one electron from the $\pi$ bonding orbitals to a $\pi$ type antibonding orbital. In acetylene, this results in the development of double bond characteristics, for example, the planar configuration with a lengthened carbon-carbon bond. In ethylene, however, the bond order drops to one and free rotation about this bond is then possible. Just as the repulsion of the antibonding orbitals ensures a trans arrangement in acetylene, so it appears in ethylene that the effect results in an equilibrium position with the planes of the $CH_2$ groups at right angles. It seems very probable that the photoisomerisation of ethylenic compounds must involve this type of mechanism.

II. 2. The presence on the oxygen atom of non-bonded electron pairs gives rise to $\pi^* - n$ transitions in the near ultraviolet spectra of carbonyl compounds. In these transitions, an electron from the non-bonded pair is excited to an antibonding $\pi$ orbital which would be expected to produce lengthening of the carbon-oxygen bond. The following analyses of molecules of this type show the effects of this kind of transition in various structures.

### II. 2(a) Formaldehyde

Attempts by several authors[22-25] to produce a comprehensive vibrational analysis of the absorption and fluorescence spectra of formaldehyde encountered serious difficulties which were largely unresolved until Walsh[26] recognised the possibility of a non-planar excited state. This concept was used by Brand[27] to give a satisfactory analysis of the vibrational structure of the near-ultraviolet spectra. The conclusion that the molecule was non-planar in the excited state was confirmed by the high resolution work of Robinson and Di Giorgio[28].

In the fluorescence spectrum, a progression in the ground state carbonyl stretching frequency is particularly marked but there are two additional progressions each based on the same interval of 2322 $cm^{-1}$. Since this interval is greatly altered by deuterium substitution, it must be associated with a hydrogen deformation vibration. A coriolis perturbation of the rotational structure of the bands of these two progressions identifies the vibration beyond doubt as the 1166 cm.$^{-1}$ out-of-plane deformation $\nu_6''$ since the same perturbation can also be identified in association with $\nu_6''$ in the infrared spectrum.

In the absorption spectrum, these two progressions in intervals of $2\nu_6''$ are absent and $\nu_6'$ plays no important part in the structure of the spectrum. Indeed the only feature in common between the fluorescence and absorption spectrum is the carbonyl progression and one band '$\alpha$', that of highest frequency in the fluorescence spectrum. In absorption, this band appears 1280 cm.$^{-1}$ to the red of the first band 'A' of the upper state carbonyl progression. Subtracting the value of $\nu_6''$ we obtain 115 cm.$^{-1}$ in agreement with the value of 113 cm.$^{-1}$ which was found to be the separation of two fluorescing levels from which originated the two progressions in $2\nu_6''$ in the fluorescence spectrum. The explanation of this 115 cm.$^{-1}$ interval, (actually 125 cm$^{-1}$ measured to the band centre) which is the link between the fluorescence and absorption spectra, proved, at first, difficult. Another problem was the prominence of $\nu_6''$ in the fluorescence spectrum in contrast to the small part played by $\nu_6'$ in the absorption spectrum. It was thought that two transitions might be responsible. However, the rotational constant $\frac{1}{2}(B' + C')$ was found to be 1.007 cm.$^{-1}$ for both $\alpha$ and A bands which was a convincing demonstration that both bands belonged to the same transition.

A comprehensive analysis embracing all details of both fluorescence and absorption spectra is possible, however, if it is assumed that the molecule adopts a slightly non-planar configuration in the excited state.

There will then be a small energy barrier to inversion, resulting in quite large splitting of even the v = 0 and v = 1 levels. The 125 $cm^{-1}$ separation then appears as the separation of the $0^+$ and $0^-$ levels from which the two progressions in $2\nu''_6$ originate. The upper state frequency of $\nu'_6$ is not important in absorption as the energy barrier is low and the levels above it rapidly become evenly spaced and characteristic of a normal harmonic vibration of a planar configuration. The band A is then due to the transition from the vibrationless ground state ($A_1$) to the $0^-$ level of the state ($B_1$) and is vibronically allowed. The band α is due to the transition between the first quantum level of $\nu''_6$ ($B_2$) and the $0^+$ level of the upper state ($A_2$) and is also vibronically allowed. The pure electronic jump from the vibrationless ground state $A_1$ to the $0^+$ level of the upper state ($A_2$) is forbidden but has been observed as a weak band 'a' to the red of band A in the absorption spectrum. The bands α and A are type B but band a is type A and is thought to be due to an allowed magnetic dipole transition. See fig. 5.

Analysis of the rotational structure reveals that the out-of-plane angle is about 20° and the carbonyl bond length is 1.32 Å. A negative value is obtained for the inertial defect which further substantiates the non-planar excited state.

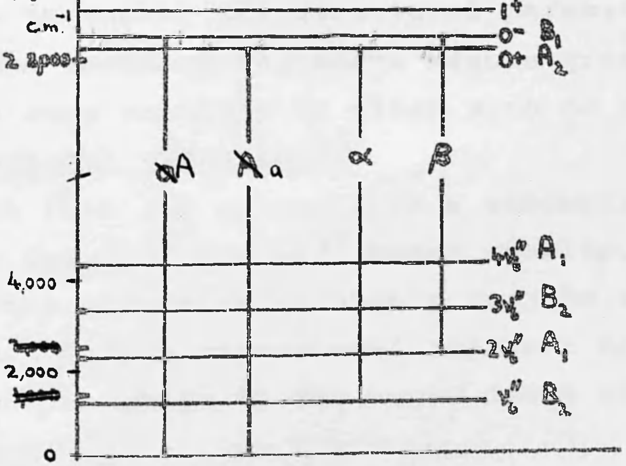


Fig. 5.

## II. 2(b) Formyl Fluoride[29, 30]

On the basis of the Franck-Condon principle, the presence in the near ultraviolet spectrum of formyl fluoride of important progressions in both the out-of-plane C-H bending vibration and the FCO in-plane angle deformation vibration is indicative of a non-planar excited state. The most important progression, however, is that of the carbonyl stretching vibration which falls to 1111 $cm^{-1}$ in the excited state suggesting, as in formaldehyde, a substantial increase in the carbonyl bond length. In all these progressions, the intensity maximum is situated at some distance from the origin which supports the suggested changes in molecular geometry.

The analysis of the partially resolved rotational structure reveals that the smallest moment of inertia increases by 30% on excitation while the average of the other two remains practically unchanged. These results are consistent with a non-planar configuration for the excited state in which the carbon-oxygen bond has increased by 0.18 $\overset{o}{A}$ and the FCO angle has decreased by about 13°. Since no evidence of inversion doubling is apparent it is reasonable to suppose that the deviation from planarity is greater than 20° although it must be less than 40° to be consistent with the moments of inertia. Insufficient data is available to enable all structural parameters to be calculated and those quoted above assume ground state values which seem unlikely to alter much on excitation.

## II. 2(c) Carbonyl Chloride[30]

The fact that the molecule is a strongly asymmetric top and that the $Cl^{35}$ and $Cl^{37}$ bands overlap, results in a rotational fine structure so highly complex as to be unresolvable. Only a vibrational analysis is then possible and the principal guide to the upper state structure is the

Franck-Condon principle. Apart from the usual carbonyl progression, two other progressions are apparent and these have been assigned to the upper state out-of-plane and in-plane bending vibrations from which it would appear that the molecule is non-planar and has different OCCl angles in the excited state. As in the case of the formyl fluoride spectrum, the bands of maximum intensity are well removed from the origin. It is possible then, that in the excited state both mirror plane symmetry elements are destroyed and the carbon-oxygen bond is lengthened. A high barrier to inversion would be expected for a pyramidal configuration and in fact no evidence of inversion doubling is apparent.

### II. 2(d) Acetaldehyde

The near-ultraviolet spectrum has been studied by a number of workers both in absorption[31,32] and in emission[33,34] but as yet no definite information has been obtained apart from the identification of the carbonyl stretching vibration which again predominates in the spectrum. Innes[32] has suggested that the molecule may have a non-planar C-C-O skeleton.

### II. 3(a) Glyoxal

Although a number of vibrational fundamentals appear in the near ultraviolet spectrum[35], the only one which forms a progression of more than two members is the carbonyl stretching vibration. The C-H wagging frequency is active but only for a change of one quantum. Sequences of the torsional frequency are associated with the carbonyl progression. It therefore appears that there is little change in the molecular geometry on excitation. The origin is the strongest band in the spectrum which supports this conclusion.

From the degradation of the K-structure it is evident that the smallest moment of inertia $I_a$ must decrease slightly on excitation and this effect rules out any possibility of relative rotation of the carbonyl groups about the single bond. It seems probable then that, in the excited state, the molecule remains planar but the CCO angle is increased by a small amount to account for the decrease in $I_a$. The high resolution work of King[36] confirms these findings, an increase of 3° in the CCO angle being calculated from the rotational structure of the origin. King also estimated that the C-C bond length increased while that of the carbonyl decreased. This conflicts both with the lower excited state frequency of the carbonyl vibration and with the lengthening normally encountered in the $\pi^*$ - N transitions of carbonyl compounds. However the evidence for the postulated contraction is, as King points out, not at all conclusive.

The spectrum of acrolein is very similar to that of glyoxal and we shall consider the glyoxal spectrum in more detail in a later section.

### II. 3(b) Biacetyl

The crystal spectra of this compound obtained at temperatures of 20°K and 40°K turn out to be sharper than the vapour spectra and are used in preference in the most recent work, which includes both emission and absorption spectra[37]. The relationships between some of the emission and absorption systems are still far from clear and it is obvious that several transitions are involved. In only two cases has it been possible to assign band systems to specific transitions. In both these cases it seems probable that there is little change in geometry on excitation.

### II. 3(c) Oxalyl Chloride

The near ultraviolet spectrum consists of a series of bands superimposed on a continuum. The intensities of these two components vary with temperature and Sidman[38] has proposed that the trans form is responsible for the band system while the cis-form gives rise to the continuum. Saksena and Jauhri[39], however, claim that both forms contribute to the band system. In these circumstances no definite analysis can be made.

### II. 3(d) Propynal[40]

The predominant feature of the near ultraviolet spectrum is the progression in the carbonyl stretching frequency, the origin being the most intense band. Although many other fundamentals have been identified in the spectrum, none form progressions of more than two members and from this evidence it appears that no major change in geometry occurs on excitation. The only large change in structural parameters is the extension of the carbonyl bond by 0.11 Å which is normal in the $\pi^* - n$ transition of carbonyl compounds. These conclusions are consistent with the rotational constants derived from the remarkably sharp fine structure. Although the out-of-plane CHO vibration is anh II. 3(c) Crotonaldehyde[41] y that the out-of-plane angle probably does not exceed 4°.

### II. 3(c) Crotonaldehyde[41]

Only the carbonyl vibration, which is responsible for the only progression in the spectrum, can be assigned. A number of other intervals have been found but the large number of possible fundamentals, the low symmetry and the diffuse bands make further progress impossible.

We see then that, in general, the simple non-conjugated carbonyl compounds are frequently forced to adopt different configurations on excitation while in conjugated carbonyl compounds the changes brought about by excitation are much less drastic. Further discussion of this subject will be postponed until chapter V so that the results of the present study of acrolein may be considered.

## III. PREVIOUS SPECTROSCOPIC STUDIES OF ACROLEIN

The first detailed observations of the electronic spectrum of acrolein were made in 1926 by Luthy[42] whose measurements were made both in the vapour phase and in solution. The solution spectra in the range 4,000 - 2,080 Å showed two distinct regions of absorption, the first being a weak band at 4000 - 2800 Å and the second a very intense band with a maximum at 2080 Å. In the vapour spectrum of the first band Luthy measured about 300 bands of the fine structure and noticed a constant separation of 1260 $\text{cm}^{-1}$ between the strongest of these bands.

In 1934 Thompson and Linnet[43] confirmed these observations and suggested that the 4,000 - 2,800 Å band and the intense band at 2080 Å were due to excitation of the carbonyl and vinyl groups respectively. The same frequency difference of 1260 $\text{cm}^{-1}$ between the strong sub-bands of the first absorption region was also observed and this was interpreted as a progression in the upper state carbonyl stretching vibration.

Using an instrument of greater resolving power, Eastwood and Snow[44] were able to examine in detail the fine structure of the bands of the carbonyl progression. It was found that for the nine bands considered, the series of lines forming the fine structure could be represented in each case by a single parabolic formula representing an isolated R-branch. It was found, however, that the rotational constants obtained from these equations were not consistent. These details of the spectrum led Eastwood and Snow to the conclusion that the excited state electronic structure of C - CHO in acrolein differed substantially from that in saturated aldehydes such as acetaldehyde. Two upper state vibrational fundamentals were identified. One, of frequency 1270 cm.$^{-1}$, was assigned to the carbonyl stretching mode in agreement with Thompson and Linnet and the other, of frequency 500 cm.$^{-1}$ was attributed to the O = CH - CH angle deformation.

Absorption to the red of the first band of the carbonyl progression was also recorded. Three bands in this region were similar in type to the main bands already considered but others were of a completely different appearance and these were assigned to a different electronic transition. No discussion of these bands or of the many continuous parallel bands which do not form part of the main progression was attempted.

The other electronic transitions of acrolein were considered in more detail by Walsh[45] who distinguished six bands in the ultraviolet spectrum of acrolein, and assigned them as below:

| | |
|---|---|
| 3300 Å | $\pi^* - n$ |
| 1935 | $\pi^* - \pi$ |
| 1750 | $\sigma - n$ |
| 1640 | Rydberg |
| 1480 | $\pi^* - \pi$ |
| 1460 | |

Nagakura[46] interpreted the 1935 A $\pi^* - \pi$ transition as a charge transfer band. The calculated contributions of the charge transfer configuration were found to be 5% and 65% for the ground and excited states respectively.

A further examination of the $\pi^* - n$ band by Inuzuka[47,48] confirmed Eastwood and Snow's assignments of the 1270 cm.$^{-1}$ and 500 cm.$^{-1}$ upper state vibrational fundamentals and, in addition, revealed two other fundamentals of frequency 1127 cm.$^{-1}$ and 1414 cm.$^{-1}$. These were assigned to the C-C and C = C stretching modes respectively. The bands to the red of the origin at 25851 cm.$^{-1}$ were interpreted as hot bands.

As in previous studies no attempt was made to deal with the continuous parallel bands.

Earlier workers had assumed a planar configuration for acrolein with the oxygen and terminal carbon atoms trans with respect to the C - C single bond and this view was confirmed in 1950 by the electron diffraction work of Mackle and Sutton [49]. The study of the microwave spectrum of acrolein by Wagner, Fine, Simmons and Goldstein [50] in 1957 provided more accurate values for the structural parameters of acrolein. A value of 2.3k. cal/mole for the cis-trans energy barrier was obtained. More detailed and precise thermodynamic constants were made available by the ultrasonic absorption work of de Groot and Lamb [51] who obtained values for the activation energies of the cis and trans conformations. Their results are shown diagrammatically in fig. 6.

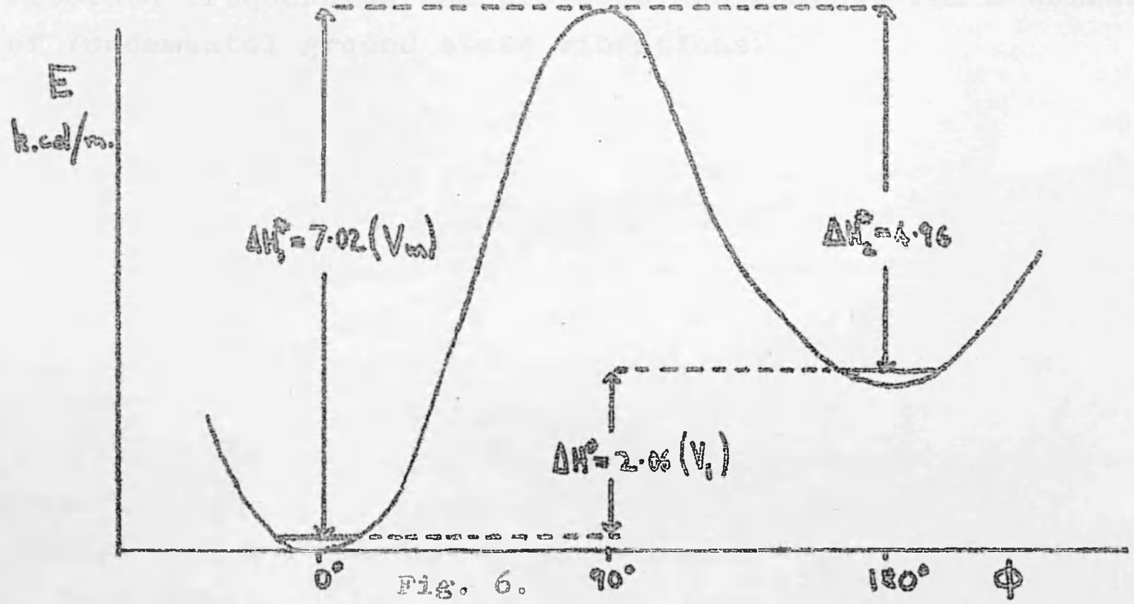


Fig. 6.

The study ofthe vibrational spectrum of acrolein was initiated in 1935 by the work of Bourgel and Piaux [52] on the Raman spectrum which was observed in the region 330 - 1700 $cm^{-1}$. Little was possible in the way of assignment but certain bands were correctly associated with the vinyl group. Similarly in the infrared work of Cotton[53] only a limited number of bands were observed and two were assigned. Further work was limited to the carbonyl stretching vibration for which the force constant and frequency were calculated[54]. The observed frequency of this band in solution and in the vapour phase was recorded. Apart from a few additional bands recorded by Davidson and Bates[55] in 1953, it was not until 1956 that the first complete infrared spectrum of acrolein was obtained. This work, by Pierson, Fletcher and St. Clair Gantz[56], was performed at moderate resolution and did not attempt an analysis of the spectrum. Additional work on the Raman spectrum appeared in 1956[57] and 1958[58] but this was concerned mainly with band intensities and the relationship of these to conjugation. In connection with his analysis of the ultraviolet $\pi^* - n$ transition, Inuzuka[48] recorded frequencies and proposed assignments for a number of fundamental ground state vibrations.

# IV. EXPERIMENTAL

## IV. 1. General

At an early stage in the analysis of the acrolein spectrum it was decided to attempt the synthesis of two deuterated derivatives of acrolein as the spectra of these molecules would assist in the assignment of both the infrared and ultraviolet spectra. The two molecules chosen were acrolein - $d_1$ $CH_2 = CH - CDO$ and acrolein - $d_3$, $CD_2 = CD - CHO$. In the case of the acrolein - $d_1$, it was hoped that the deuterium could be introduced by reducing an acrylic acid derivative with lithium aluminium deuteride[59]. The most direct method, that of reducing acrylonitrile to the aldehyde using $\frac{1}{4}$ mole of the deuteride for each mole of nitrile[60] did not give any appreciable yield of acrolein. Although involving an additional stage and requiring larger quantities of deuteride, synthetic routes, which have allyl alcohol as the precursor of acrolein, possess the considerable advantage of affording an excellent means of purifying the product. The purification of small samples of acrolein to the standards required for infrared spectroscopy is difficult as the compound polymerises very rapidly at room temperature. This behaviour precludes the use of such techniques as distillation or vapour phase chromatography. Since the only impurities introduced by the oxidation techniques described below are water and permanent gases, purification can therefore be carried out at the alcohol stage. This is particularly suitable since it has been found that allyl alcohol can be easily purified by vapour phase chromatography. This method is of great sensitivity, does not expose the compound to prolonged high temperatures and is ideally suited to the handling of small quantities. In this way, a very pure sample of allyl alcohol can be prepared. Oxidation of this sample produces a sample of acrolein which merely requires drying and vacuum distillation to bring it to a similar standard of purity. Two samples of normal acrolein were used for the spectroscopic measurements. A sample of commercial acrolein was dried (anhydrous magnesium sulphate) and subjected to a number of vacuum distillations and a second sample was synthesised from acrylic acid via the anthracene adduct as described below. Comparison of the two infrared spectra enabled any remaining weak impurity bands to be eliminated.

In view of the failure of the direct reduction of acrylonitrile to acrolein, the route now envisaged was that of reduction of an acrylic acid derivative with lithium aluminium deuteride followed by oxidation of the resulting deuterated allyl alcohol to the aldehyde. It was found that acrylyl chloride gave the best yields of alcohol on reduction although these were low due to the formation of saturated by-products. Vapour phase chromatography of the product, using a 3 feet 20% 'Carbowax 600' column in a Griffen & George V.P.C. Apparatus Mk II, gave a pure sample of the alcohol. Attenburrow[61] had reported a high yield of acrolein from allyl alcohol using the manganese dioxide allylic oxidation method. However, in that case, the acrolein was isolated as the 2:4 - dinitrophenylhydrazone derivative and the yield of acrolein calculated from the weight of derivative obtained. In fact it was found impossible to extract the free acrolein from the reaction mixture without contamination by light petroleum. As the reaction mixture could not be fractionated or given V.P.C. treatment because of polymerisation difficulties the only method available was that of removing the acrolein under reduced pressure from the cooled reaction vessel. To avoid contamination, high boiling point petroleum ether had to be used and it was found that the yields were considerably reduced. In view of these difficulties, the chromium trioxide method of Wille and Saffer[62], was used. However, the overall yield for the synthesis was only of marginal utility considering the small quantities of lithium aluminium deuteride available.

In order to improve the yield of deuterated allyl alcohol, the carbon-carbon double bond of methyl acrylate was protected by forming the Diels-Alder adduct with anthracene as the diene[63]. This adduct, methyl 9:10 - ethanoanthracene - 11 - carboxylate, was then reduced with lithium aluminium deuteride[63] and the resulting alcohol, a highly crystalline solid, on heating to 370° decomposed to give allyl alcohol and anthracene in high yield. A fundamental difficulty in the oxidation of the allyl alcohol is the kinetic isotope effect. The rate of removal of deuterium from the substrate is seven or eight times slower than for hydrogen removal. Effectively, this means greatly increased attack on the carbon-carbon double bond and in practice yields are drastically reduced. This difficulty was overcome by developing the gas phase catalytic method originated by Jong and Groll[64,65]. This method eliminated attack on the carbon-carbon double bond, permitting only the specific oxidation of hydroxyl to carbonyl. This kind of specificity, coupled with the use of large catalyst surface areas and slow flow rates, enabled the adverse isotope effect to be overcome.

With these improved methods, adequate quantities of pure acrolein and acrolein - $d_1$ were prepared.

The characteristic properties of the ethynyl group rendered it extremely convenient as a means of synthesising acrolein - $d_3$, and propargyl alcohol was the most suitable compound. In the first instance, a deuterium atom could be substituted merely by exchanging the acidic hydrogen atom in deuterium oxide in the presence of a trace of base. Secondly, the remaining deuterium atoms in the desired vinyl group could be inserted by reduction of the ethynyl group. This reduction could be achieved either by use of catalytic hydrogenation techniques, merely substituting deuterium for hydrogen, or by a purely chemical reduction using lithium aluminium deuteride. This reagent specifically reduces carbon-carbon triple bonds to double bonds in the presence of an $\alpha$ - hydroxyl[66] substituent which condition is fulfilled in this case. Preliminary experiments showed that the hydrogenation of propargyl alcohol using 'Lindlar' catalyst did not stop at the double bond stage and, on stopping the reaction after the uptake of the theoretical volume of hydrogen, it was found that a number of products, including propargyl, allyl and propyl alcohols, were present. The low yield of allyl alcohol and the severe contamination made this method unacceptable. However, the reaction of lithium aluminium hydride with propargyl alcohol gave a 65% yield of allyl alcohol which could then be purified as previously described. When the reaction was carried out using deuteride in place of hydride and propargyl alcohol - $d_2$ and the resulting allyl alcohol oxidised catalytically to acrolein it was found that the sample contained 12% acrolein, 27% acrolein - $d_1$, 52% acrolein - $d_2$ and only 3% acrolein - $d_3$.

It seemed that two possible sources of the unwanted hydrogen existed. The rate of exchange of deuterium and hydrogen at the hydroxyl site is so great that, without developing special equipment, it was impossible to achieve a deuterium concentration in excess of 70% although 95% was obtained for the ethynyl position. The remaining hydrogen could have exchanged with the deuteride during the reduction and thus entered the vinyl group. It is also possible that, during the catalytic oxidation, some deuterium from the vinyl group may have exchanged with hydrogen absorbed on the catalyst surface. In order to eliminate this possibility the experiment was repeated reverting in this case to the chromium trioxide method of oxidation. As the deuterium is confined to the vinyl group, its effect on the rate of oxidation is slight and a yield of 35% acrolein was obtained. In this case the composition of the product was approximately two thirds acrolein - $d_2$, one third acrolein - $d_1$ and a small amount, 5 - 10%, acrolein $d_3$. While this was an improvement, it was still obvious that hydrogen was entering the vinyl group most probably during the reduction.

In order to remove this source of hydrogen it was proposed to perform a similar reduction on propargyl acetate, deuterated at the ethynyl position. This should yield allyl alcohol - $d_3$ and ethanol - $d_2$. Although more wasteful in terms of expenditure of lithium aluminium deuteride, this method offered the advantage of excluding hydrogen vigorously. A preliminary experiment with the hydrogen compound gave a 50% yield of allyl alcohol. When the experiment was repeated with the deuterium compounds a 45% yield of allyl alcohol was obtained which, on oxidation, gave a similar range of products to that obtained in the previous synthesis. At this stage attempts were made to determine the distribution of deuterium in the molecule by nuclear magnetic resonance spectroscopy. It was found that, due to complex spin-spin coupling resulting from the conjugated double bond system, the multiplet bands obtained were too complex for analysis. The sample was therefore brominated and the N.M.R. spectrum of 1:2 - dibromoacrolein was compared with that of an authentic sample. By this means, it was discovered that each proton site in the molecule, including the formyl position, contained the same proportion of deuterium. Further discussion of this problem and details of the N.M.R. spectra will be found in Section VI.

## IV. 2. Organic Syntheses

### Acrylyl Chloride[67]

Sodium acrylate (27g, 0.29 moles) was ground to a fine powder and suspended by vigorous stirring in high boiling pet. ether (100 mls.) contained in a 250 ml. three-necked flask fitted with a dropping funnel and protected against moisture. The flask was cooled in an ice bath and phosphorus oxychloride (16 g., 0.18 moles) was added dropwise over half-an-hour. The temperature was allowed to rise to room temperature and stirring was continued for a further half-hour. The reaction mixture was then fractionally distilled and the fraction boiling in the range 72-74° was collected. The yield of acrylyl chloride was 15 g., 57%.

### Allyl Alcohol

Lithium aluminium deuteride (3 g., 0.071 moles) was dissolved in sodium dried ether (250 ml.) contained in a one litre three-necked flask by refluxing and stirring for three hours. The apparatus was flushed with a stream of rigorously dried nitrogen during the whole process. The flask was cooled in an ice-salt bath and acrylyl chloride (14 g., 0.15 moles) was added dropwise to the stirred solution of lithium aluminium deuteride. After the addition of the chloride, which required about 45 minutes, the flask was allowed to warm up to room temperature and was stirred for a further hour. The complex formed was then decomposed with sulphuric acid (250 mls., 10%) and the ether layer separated off. The aqueous layer was extracted with 8 50 ml. portions of ether and the combined ether extracts dried (anhydrous magnesium sulphate). The ether was then removed and the residue chromatographed on the Griffen and George V.P.C. Unit in 0.5 ml. portions. The conditions were: Flow 3.1 l. $N_2$/hour, Temperature 83°

Inlet Pressure 46 cm Hg.
Outlet Pressure 37 cm Hg.
Sensitivity x 1.

The peak due to the allyl alcohol was identified by its characteristic retention time (previously obtained from control samples) and only material corresponding to this peak was collected. The yield of pure allyl alcohol - $d_2$ was 1.5 g., 16.7%.

Acrolein - $d_1$

A solution of chromium trioxide (2.1g.) in water (13 ml.) and sulphuric acid (1.4 ml.) was added slowly over 45 minutes to a solution of allyl alcohol - $d_2$ (1.5 g.) in water (8 ml.) and sulphuric acid (1.3 ml.). The pressure in the flask was maintained at 50-60 mm. by a water pump and fine nitrogen leak which allowed a stream of gas to pass through the liquid. The flask was cooled in an ice-salt bath and a liquid air trap was incorporated in the vacuum system between the pump and the flask. After the addition of the chromium trioxide solution, the nitrogen leak and reduced pressure were maintained for a further hour after which the cold trap was transferred to a vacuum line. After degassing, drying and the removal of carbon dioxide, it was found that only a trace of acrolein had been obtained.

## Methyl 9, 10 - ethanoanthracene - 11 - carboxylate

Anthracene (20 g., 0.112 moles) and methyl acrylate (30 g., 0.35 moles) were dissolved in nitrobenzene (250 ml) and the solution refluxed for 6 hours. The solution was then concentrated by the removal of nitrobenzene and excess ether under reduced pressure. When the volume had been reduced to about 50 ml the solution was cooled in an ice bath and ether (50 ml) added. On shaking, a mass of crystals separated and were filtered off and washed with small portions of ether. A yield of 13 g., 45% of colourless crystals M.Pt. 116-117°C. was obtained. The infrared spectrum is shown in fig. 8

## 9, 10 - Ethanoanthracene - 11 - methanol

Lithium aluminium hydride (1 g., 0.026 moles) was dissolved in sodium dried tetrahydrofuran (600 ml) by stirring and refluxing for 3 hours. A solution of methyl 9, 10 - ethanoanthracene - 11 - carboxylate (9.29 g., 0.035 moles) was added slowly to the refluxing solution of the hydride. Reflux and stirring were continued for 16-18 hours and then sulphuric acid (10%, 150 ml) was cautiously added. The tetrahydrofuran was removed under reduced pressure and the dilute sulphuric acid extracted with 4 150 ml portions of ether. The combined extracts were washed with sodium carbonate solution and dried over anhydrous potassium carbonate. The bulk of the ether was removed and the concentrated solution set aside to crystallise slowly. Large rhombic colourless crystals were obtained M.Pt. 108-110°C. (Lit. 110°C.). A mixed melting point with the ester lowered the melting point to 90-94°C. The infrared spectrum showed no carbonyl peak and a hydroxyl peak had appeared. The total yield was 7.4 g., 88%. The infrared spectrum is shown in fig. 9.

## Allyl Alcohol

9, 10 - Ethanoanthracene - 11 - methanol (6.43 g., 0.027 moles) was placed in a 100 ml round bottom flask to which was attached a 15 cm. vacuum jacketed vigreux column. The side arm led directly to a receiver adaptor and flask which was cooled in powdered solid carbon dioxide. A Wood's metal bath was heated to 350-360°C. and the whole assembly lowered so that the level of metal was above the level of the alcohol which had been previously melted in the flask. After 4-5 minutes distillate appeared at the rate of 1 drop/10-8 secs. When the rate had dropped to 1 drop/minute, distillation was stopped. The boiling point of the liquid was 90°C. and the yield 1.16 g., 75%. The infrared spectrum showd that the liquid was a pure sample of allyl alcohol.

## 9, 10 - Ethanoanthracene - 11 - methanol - 13 - $d_2$

The reaction was carried out exactly as for the hydrogen analogue except that lithium aluminium deuteride (1 g., 0.024 moles) was used in place of the hydride and a yield of 7.29 g., M.Pt. 110°C. was achieved. This had the infrared spectrum shown in fig. 10.

The 9, 10 - ethanoanthracene - 11 - methanol - 13 - $d_2$ (7.29 moles) was pyrolysed as previously described and a yield of allyl alcohol - $d_2$ of 1.548 g., 86% was obtained. Oxidation by the chromium trioxide method again yielded negligible quantities of acrolein - $d_1$.

## Catalytic Oxidation of Acrolein

A 35 cm. roll of fine copper gauze was packed in a glass tube and maintained at 450°C. in a stream of oxygen for 3 hours. The temperature was lowered to 200° and hydrogen passed through the tube for a further three hours. This cycle was repeated about four times. Starting with a freshly reduced surface maintained at 320°C., air was drawn through the system slowly by a water pump. Allyl alcohol was allowed to fall drop by drop on to a glass fibre mat on top of the vertical catalyst column. The alcohol vapourised on the mat and passed through the catalyst column mixed with air. A cold trap was situated in the system on the outflow side of the column. After the allyl alcohol had been added the experiment was discontinued and the cold trap transferred to the vacuum line. By measuring the volume and pressure of the vapour after removal of water, carbon dioxide, etc., a yield of 55% of acrolein was estimated. It was found that only the top 5 cm. of the catalyst column were blackened at the end of the experiment.

## Acrolein - $d_1$

A further sample of 1.175 g. of allyl alcohol - $d_2$ was obtained by the anthracene adduct method and was purified by vapour phase chromatography. The apparatus was modified so that the V.P.C. cold trap could be fitted directly into the oxidation system and the pure sample was vapourised by a stream of preheated air. As described above, a yield of 0.38 g., 34% of acrolein - $d_1$ was obtained. It was noticed at the conclusion of the experiment that the blackening of the catalyst on this occasion extended almost to the foot of the column.

## Hydrogenation of Propargyl Alcohol

Propargyl alcohol (1.03 g.) was hydrogenated using 0.13 g. of Lindlar catalyst which took up 10 mls of hydrogen on presaturation. The solvent was n-amyl acetate (50 mls). Over four hours, 437 mls. of hydrogen, the theoretical amount for one double bond, were taken up. At this point the reaction was stopped and the catalyst filtered off. The solution was fractionally distilled to give two main components, one in the range 86-92°C. and the other in the 136-8° region. The lower boiling fraction 0.632 g., 56% was subjected to V.P.C. analysis and showed a wide range of products. The proportion of allyl alcohol was small and propargyl and propyl alcohols were also present. These components were identified by their retention times under standard conditions.

## Lithium Aluminium Hydride reduction of Propargyl Alcohol

Propargyl alcohol (2 g., 0.036 moles) in ether (60 ml) was added dropwise over an hour to a stirred, refluxing solution of lithium aluminium hydride (2 g., 0.053 moles) in ether (250 ml). The apparatus was flushed with a slow stream of dry nitrogen. Refluxing and stirring were continued for 18 hours and saturated ammonium chloride (24 ml.) was then added cautiously. The ethereal solution was filtered off and the precipitate washed with 4 50 ml. portions of ether. The combined ether solutions were dried (anhydrous magnesium sulphate) and the ether removed. The crude product was given V.P.C. treatment and a yield of 65% allyl alcohol was obtained.

This experiment was repeated using propargyl alcohol - $d_2$ (1.2 g., 0.021 moles) and lithium aluminium deuteride (1 g., 0.024 moles). The yield of allyl alcohol - $d_3$ after V.P.C. treatment was 0.4 g., 31%.

## Propargyl Acetate - $d_1$

Propargyl alcohol (5 g., 0.089 moles) was allowed to stand for 2 hours with deuterium oxide (5 g., 0.25 moles) and sodium carbonate (20 mg.). The solution was then poured into sodium dried ether (50 ml.) and vacuum dried anhydrous sodium sulphate added slowly with shaking until all the water had been taken up. The ether solution was allowed to stand in contact with excess drying agent for 4 hours and was then filtered and the ether removed under reduced pressure.

A solution of sodium deuteroxide was prepared by adding metallic sodium (1.4 g.) in small pieces to deuterium oxide (7 g.). The apparatus was kept flushed with a rapid stream of dry nitrogen during this operation. This solution was then added slowly over half an our to a stirred solution of acetic anhydride (6 g., 0.059 moles), deuterium oxide (8 g) and the propargyl alcohol obtained as above (5 g., 0.089 moles). The reaction flask was cooled in an ice-salt bath and was rigorously protected against atmospheric moisture. After theaddition of the sodium deuteroxide the flask was allowed to warm to room temperature, stirring being maintained for a further hour. Two layers were now present and the non-aqueous layer was taken up in ether, separated, dried (vacuum dried anhydrous sodium sulphate) and the ether removed. Distillation of the crude ether gave a yield of 3 g., 34.5% of pure propargyl acetate, B.Pt. 116-118°C. From the infrared spectrum, the deuterium content at the ethynyl position was estimated to by 87%.

## Reduction of Propargyl Acetate - $d_1$

Propargyl acetate (2.4 g., 0.024 moles) in 100 ml. ether (sodium dried and distilled from $P_2O_5$) was added slowly over ~~half-an-hour~~ to a refluxing, stirred solution of lithium aluminium deuteride (2 g., 0.048 moles). The refluxing and stirring were continued for a further 17 hours after which a saturated solution of ammonium chloride (10 mls.) was added cautiously to the solution. The ether solution was filtered and dried (anhydrous magnesium sulphate). The ether was removed and the residue chromatographed using two 3 ft., 20% carbowax '600' on brickdust, columns. A yield of 0.6 g., 45% allyl alcohol - $d_3$ was obtained. Three other products were also obtained in smaller quantities. Propargyl and ethyl alcohols were identified but propargyl acetate was absent.

## IV. 3. Spectroscopic Details

The infrared spectra were recorded with a Unicam S.P. 100 spectrometer. In the 3,600 - 650 cm.$^{-1}$ range, the instrument was operated as a NaCl prism-diffraction grating double monochromator and, in the 700 - 400 cm.$^{-1}$ range, as a KBr prism monochromator. Slit widths in the 3,600-1,700 region were about 5 or 6 cm.$^{-1}$, those in the 1,700-700 region about 2.5-4 cm.$^{-1}$ and in the KBr prism range approximately 3 cm.$^{-1}$. The spectra were calibrated for each change of prism cam throughout the entire range 3,600-400 cm.$^{-1}$ using the vapour spectra of carbon monoxide, methane, hydrogen chloride and bromide, water, ammonia and trichlorobenzene as references. Apparent molecular extinction coefficients were calculated for the principal bands. Vapour pressures varying from 5 to 120 mm. of Hg in a gas cell of path length 100 mm. were required to cover the range of band intensities adequately.

The ultraviolet absorption spectra were recorded in the range 3,600-4,150Å on Kodak B.10 photographic plates using a Hilger medium glass spectrograph. The dispersion at the plate was 9Å/m.m. at 3,800Å. Some low resolution ultraviolet spectra were obtained with an automatic recording, double beam Perkin Elmer Model 137 ultraviolet spectrometer. Slit widths were usually 20-25$\mu$ but in order to penetrate to 3,600Å and further to the violet, slit widths of up to 50 μ were used for some plates. Absorption paths ranging from 0.004 to about one metre atmosphere and exposures of 10 secs. to 3½ hours were required for complete coverage of the spectrum within the stated limits. The source used was a 12 volt tungsten filament lamp. Calibration spectra from an iron arc were placed immediately above the absorption spectra. Frequencies were determined with a Pye comparator and a Hilger non-recording microphotometer, the iron arc spectrum serving as a reference.

N.M.R. spectra were obtained using an A.E.I. R.S.2. spectrometer operating at 60 megacycles.

## V. RESULTS AND DISCUSSION

### V. 1. Infrared Spectra

The electron diffraction, microwave and ultrasonic studies show quite definitely that the acrolein molecule in the ground state is planar with the two multiple bonds disposed in a trans relation to the carbon-carbon single bond. The molecule thus possesses a plane of symmetry and so belongs to the point group $C_s$. Of the eighteen normal co-ordinates which characterise the vibration of the eight atoms of the molecule, thirteen, being located in the symmetry plane, are therefore unchanged by the operation of reflection in the plane and are characterised by the totally symmetric symmetry species $A'$. The remaining five normal co-ordinates describe out-of-plane vibrations, changing direction but not magnitude on reflection in the plane and so are characterised by the non-totally symmetric species $A''$.

The molecule is a near symmetric top with the asymmetry parameter $\kappa = -0.98$ and $I_a = 10.52$, $I_b = 108.42$, $I_c = 118.94$ a.m.u. $\mathring{A}^2$. It has been described how the rotational structure of a band may be used to ascertain various details of the transition. However, with the resolution available, it was possible only to distinguish the band envelope and, in favourable cases, the $K$-structure. In these circumstances it is still possible, as we have seen, to deduce the direction of the transition moment. The use of band envelopes in this way is of considerable value, as will become apparent, in the assignment of the infrared bands of acrolein. We have pointed out that the structure of a band envelope arising from the transitions of a symmetric top will, in the slightly asymmetric case, be modified near the band centre. In acrolein, the a-axis corresponds to the top axis and type A bands then correlate with the parallel bands of a symmetric top. Similarly type B and C bands are related to the perpendicular bands. The effect of the asymmetry on the parallel type is not marked and type A bands possess a central peak of moderate intensity. For perpendicular bands the changes brought about by the introduction of a small degree of asymmetry are more pronounced. There are, of course, two possibilities corresponding to type B and type C bands. In the former, a central minimum is developed but in the latter the opposite effect occurs and the sub-bands move toward the band centre resulting in the formation of a very strong central maximum. The parts of the band outside of this central region retain the normal parallel or perpendicular structure and are relatively unaffected by slight asymmetry.

If we now summarise the features of each type of band envelope it is obvious that each type possesses distinctive characteristics.

Type A: Weak central branch, No K structure
Type B: No central branch, Prominent K structure
Type C: Intense central branch, Prominent K structure.

By this means it is possible to separate the bands due to the two symmetry species. The non-totally symmetric $A''$ vibrations are those which are out-of-plane and consequently give rise to type C bands since the direction of the transition moment in these cases must be along the c-axis. The totally symmetric $A'$ vibrations will of course give rise to type A and B hybrid bands.

Since all the nuclear displacements in the plane of the molecule have components along both the A and B axes of inertia, pure type A and type B bands are not observed and all bands are hybrid in type, being composed of varying proportions of type A or B character. It is not easy to estimate the predominant character of a fundamental due to the fact that the nuclear displacement concerned is never completely localised in the one bond but affects other nuclei causing small dipole moment displacements in situations remote from the principal centre of displacement. In this way, unforeseen contributions to the transition moment vector may arise. Thus, although two of the vinyl C-H bonds are in almost identical orientations with respect to the inertial axes as the formyl C-H bond, in fact type A bands are observed for the vinyl hydrogen stretching fundamentals while an almost pure type B band is observed for the similar vibration of the formyl hydrogen. Classification of bands into types A and B is not therefore a reliable guide to the assignment of fundamentals.

Another aid to the assignment of bands is the availability in the literature of a number of previous analyses of the infrared spectra of similar substituted ethylene molecules[69,70]. Characteristic frequencies for the different types of vibration associated with this general molecular structure can then be obtained.

The shifts in frequency produced when a hydrogen atom is replaced by deuterium at a known position have also proved useful in assisting the process of assignment.

All the fundamental vibrations are expected to be active in the infrared region but two lie outside the low frequency limit of the spectrometer. These are the carbon-carbon single bond torsional vibration $\nu_{18}$, estimated by the microwave workers to be 200 cm$^{-1}$, and the carbon skeleton deformation $\nu_{13}$ vibration which Bourgel and Piaux[52] found to have the frequency 335 cm.$^{-1}$ in the Raman spectrum.

Of the sixteen fundamentals in the working range of the instrument, two were not observed due to overlapping by stronger bands. Only two of the three vinyl hydrogen stretching frequencies could be measured with certainty although the third could be partially observed as a shoulder.

The out-of-plane carbonyl wagging vibration $\nu_{16}$ was not observed although it appeared as a shoulder in the 800 cm.$^{-1}$ region in the spectra of the formyl deuterated sample. From this it was concluded that in the normal spectrum it is obscured by the intense absorption in the 1100-900 cm.$^{-1}$ range. The formyl hydrogen in-plane rocking frequency drops substantially on deuterium substitution and the corresponding deuterium frequency is presumably lost under the intense absorption at lower frequencies. Apart from these few difficulties, the bands of the spectrum are well spread out and surprisingly few instances of serious overlapping of bands occur for such a relatively complex molecule.

Tables 5 and 6, Section VI list all the observed features in the infrared vapour spectra of both acrolein and acrolein - $d_1$. Figures 11-14 in the same section show typical bands. Table 3 in this section p.71 lists the frequencies of the fundamentals for both molecules, those for the normal molecule being averages of the two series of measurements mentioned in table 5.

KBr Region

Two bands, partly overlapping, occur in this region and are of two distinct types, that at 564 cm.$^{-1}$ being type A and that at 589 cm.$^{-1}$ type C. (See fig. 11). The 589 cm.$^{-1}$ band must therefore be attributed to a non-totally symmetric $A''$ vibration which, by reason of the low value of the frequency, must be the carbon-carbon double bond torsional vibration $\nu_{17}$. A vibration of the $A'$ species must be responsible for the type A band and again the low value of the frequency identified the vibration as the O = C-C skeletal deformation $\nu_{12}$. In the acrolein - $d_1$ spectrum the relative positions of these two bands are interchanged. No other bands are observed in this region.

## 700-2000 cm.$^{-1}$ Region

A group of four very strong bands again of types A and C lie between 900 and 1200 cm.$^{-1}$. (See fig. 12 and 13). The bands at 913 cm.$^{-1}$ and 1160 cm.$^{-1}$ are of type A and are assigned to the totally symmetric carbon-carbon single bond stretching $\nu_{11}$ vibration and the vinyl in-plane rocking $\nu_{10}$ vibrations respectively. A very weak band of ill-defined contour occurs at about 730 cm.$^{-1}$. Due to its weakness and lack of structure it would seem to be a combination band, possibly of $\nu_{12}$ and $\nu_{18}$. ($\nu_{12} + \nu_{18} = 721$).

The bands at 959 and 993 cm.$^{-1}$ are characterised by extremely intense central branches and well developed fine structure on the R and P branches. These two bands are therefore type C and arise from non-totally symmetric vibrations. Their characteristic frequency allows the bands to be assigned to the vinyl out-of-plane wagging and twisting vibrations respectively $\nu_{15}$ and $\nu_{14}$.

The spectrum of the formyl deuterated compound shows marked differences in this region. (See fig. 13). Understandably, $\nu_{15}$ and $\nu_{14}$ are virtually unaffected by the deuterium substitution but $\nu_{10}$ drops in frequency so that it is almost completely separated from the combined absorption of the two $A''$ fundamentals. Of course, the $A''$ carbonyl wagging vibration $\nu_{16}$ undergoes the greatest shift to lower frequencies and the strong central branch can just be discerned as a shoulder at 846 cm.$^{-1}$. (See fig. 13) All the fundamentals of species $A''$ have now been accounted for and in fact no further type C bands are observed in the spectrum.

Between 1200 and 1500 cm.$^{-1}$, the type A bands of three bending vibrations are observed. These are assigned to the vinyl in-plane rocking vibration $\nu_9$, 1276 cm.$^{-1}$ the formyl hydrogen in-plane rocking vibration $\nu_8$, 1361 cm.$^{-1}$ and the $CH_2$ = bending vibration $\nu_7$, 1422 cm.$^{-1}$. As expected, $\nu_8$ undergoes a large displacement to lower frequencies and no band is observed at 1361 cm.$^{-1}$ in the formyl deuterated case. No direct assignment has been made for $\nu_8$ and it is supposed that the fundamental, a relatively weak band, is obscured by the strong bands at lower frequencies. However the probable identification of the first overtone of this fundamental gives a very approximate position of around 1040 cm.$^{-1}$. A weak type B band at 1480 cm.$^{-1}$ is thought to be a combination band arising from $\nu_{11}$ and $\nu_{12}$ ($\nu_{11} + \nu_{12} = 1477$).

In the 1500-2000 cm.$^{-1}$ range, two stretching vibrations and a number of overtones occur. The carbon-carbon double bond stretching vibration has the typical value of 1626 cm.$^{-1}$ and the carbonyl stretching vibration is also easily identified by its characteristic value of 1722 cm.$^{-1}$ and its uniquely high intensity. The type B bands at 1824 and 1917 cm.$^{-1}$ are undoubtedly the first overtones of the $\nu_{11}$ and $\nu_{15}$ fundamentals respectively. ($2\nu_{11} = 1825.6$ and $2\nu_{15} = 1918.4$ cm.$^{-1}$). Both the fundamental bands are of high intensity which accounts for the relatively high intensity of the overtones. A weak band occurs at 2046 cm.$^{-1}$ and may be the first overtone of the strong 994 cm.$^{-1}$ $\nu_{15}$ fundamental although the agreement ($2\nu_{15} = 1988$ cm.$^{-1}$) is not good. However no other combination gives a better approximation. In the spectrum of the formyl deuterated compound, the formyl deuterium stretching vibration occurs in this region in Fermi resonance with another component which may be tentatively assigned to the first overtone of the missing deuterium rocking fundamental. The high intensity of the overtone band is indicative of strong coupling with the fundamental, suggesting a close relationship between the two vibrational modes. The present assignment fulfils this condition since the two modes proposed both involve motion of the same atom. Correction for the Fermi resonance gives values of 2079.8 and 2090.8 cm.$^{-1}$ for the stretching fundamental and the rocking overtone respectively. This value for the overtone requires the missing fundamental to have a value of about 1040 cm.$^{-1}$. There is indeed evidence of absorption at this position but it is not possible to substantiate this interpretation as the onset of intense absorption due to $\nu_{15}$ and $\nu_{14}$ occurs at this point.

A further example of Fermi resonance occurs around 1700-1750 cm.$^{-1}$ and involves the carbonyl stretching fundamental $\nu_5$ and the first overtone of the $\nu_{10}$ fundamental which acquires considerable intensity by the interaction with the strong carbonyl vibration. The corrected frequencies are 1709 cm.$^{-1}$ for the fundamental and 1746 cm.$^{-1}$ for the overtone.

## Table 3

## Fundamental Frequencies of Acrolein and Acrolein - $d_1$

All values are given in $cm.^{-1}$.

| Species | Mode | | $CH_2=CH-CHO$ | $CH_2=CH-CDO$ |
|---|---|---|---|---|
| a′ | Vinyl C-H stretching | $\nu_1$ | 3103.2 | 3101.5 |
| | " " " | $\nu_2$ | 3000.5 | 2987.9 |
| | " " " | $\nu_3$ | a | a |
| | Formyl " " | $\nu_4$ | 2799.9 | 2079.8f |
| | Carbonyl stretching | $\nu_5$ | 1722.7 | 1708.8f |
| | C = C " | $\nu_6$ | 1625.7 | 1620.5 |
| | $CH_2$ = bending | $\nu_7$ | 1421.9 | 1403.3 |
| | Formyl C-H in-plane rocking | $\nu_8$ | 1361.2 | 1040 d |
| | Vinyl " " " | $\nu_9$ | 1276.2 | 1275.2 |
| | " " " " | $\nu_{10}$ | 1159.3 | 1152.7 |
| | C-C stretching | $\nu_{11}$ | 912.8 | 876.8 |
| | O= C-C bending | $\nu_{12}$ | 563.9 | 561.8 |
| | C-C = C " | $\nu_{13}$ | 335 e | b |
| a″ | Vinyl twisting | $\nu_{14}$ | 993.3 | 992.6 |
| | " wagging | $\nu_{15}$ | 959.2 | 959.2 |
| | Formyl " | $\nu_{16}$ | a | 846.3 |
| | C = C torsion | $\nu_{17}$ | 588.8 | 555.7 |
| | C - C " | $\nu_{18}$ | 156.9c | 149.8c |

a. Obscured by intense overlapping bands.

b. Outside available frequency range.

c. Obtained from 'hot' ultraviolet bands.

d. Approximate value, estimated from overtone.

e. Obtained by Bourgel and Piaux from the Raman spectrum.

f. Corrected for Fermi resonance.

## 2000 - 3400 cm.$^{-1}$ Region

The first significant absorption above the 2000 cm.$^{-1}$ region is a group of three overlapping type B bands of high intensity and with well developed K-structure. This group, forming a three component Fermi resonance poses some problems of assignment. The formyl hydrogen stretching vibration is expected to occur in this region and might also be expected to give rise to a type B band. It therefore seems reasonable to assign the most intense member of the group at 2,800 cm.$^{-1}$ to this fundamental. The assignment of the other two bands is less certain but it is probable that the 2693 cm.$^{-1}$ band is the first overtone of $\nu_8(2\nu_8 = 2722.4)$. The central band at 2754 cm.$^{-1}$ cannot be an overtone and it is difficult to find a simple combination of fundamentals which is at all probable and yet approximates, even roughly, to the observed value. It is likely that three components are involved, quite probably including the missing and related formyl hydrogen rocking vibration. In the spectrum of acrolein - $d_1$ bands of similar type appear in almost the same positions as those assigned to $\nu_4$ and $2\nu_8$ in the spectrum of normal acrolein but are much weaker in intensity. This shows that a small percentage of normal acrolein is still present in the deuterated sample. It is interesting that the central band is absent or of lower intensity which supports the suggestion that the band involves the formyl hydrogen rocking fundamental in combination with one or more other fundamentals.

Two of the vinyl hydrogen stretching vibrations appear at 3000 and 3100 cm.$^{-1}$. Further absorption is apparent between these two bands and the third fundamental of this type presumably occurs in this region but is obscured by the other two.

All the fundamentals have now been discussed and no further strong bands are expected or observed although the carbonyl overtone at 3422 cm.$^{-1}$ is quite prominent. In the case of acrolein - $d_1$, it is accompanied by the overtone of the 2 $\nu_{10}$ band which presumably gains intensity by Fermi resonance just as in the situation around 1730 cm.$^{-1}$ with the $\nu_5$ fundamental.

Torsional Vibration

Although the frequency of the carbon-carbon single bond torsional vibration is expected to lie well outside the range of the infrared spectrometer, it has been possible to obtain fairly accurate values since this fundamental is active in the ultraviolet spectrum. In the course of the analysis of the ultraviolet spectra the ground state and upper state values for this fundamental in both acrolein and acrolein - $d_1$ have been obtained, and are shown in table 3. Using the method of Pitzer[71,72] and the thermodynamic data of de Groot and Lamb[51] the values of these fundamentals for the two isotopic molecules have been calculated independently of any spectroscopic measurement and the results show excellent agreement with those obtained from the ultraviolet spectra. This topic will however be considered in greater detail in the next section.

## V. 2. Ultraviolet Spectra

### (a) The Triplet System

To the red of the origin of the well established 3,867Å transition, a very weak band system extends to longer wavelengths. Using a multiple reflection cell, path lengths of 5 metres of the saturated vapour at about 150 m.m. pressure were required for adequate coverage of the system. The bands of this weak system appear to be of two types and are completely different in appearance from the bands of the 3,867Å transition. The more intense of the two types of bands strongly resemble the hybrid type of infrared band, being characterised by a weak central maximum. No evidence of K-structure is apparent. Presumably the bands are mainly type A. The other type of band in this system is distinguished by a central minimum. It is possible that fine structure may be associated with these bands but, even with 5 metre path lengths, their intensity was never sufficient to allow a detailed examination to be made. Figs. 17 and 18 show some of these bands.

Inuzuka[48] has interpreted the system as a series of hot bands related to the 3867Å singlet system but did not observe any of the hot bands described in the next section (V. 2(b)) and also by Eastwood and Snow.

Compared with the 3867Å transition, this system has a much lower intensity, as a whole, and also entirely different band envelopes. It is concluded, therefore, that this system is due to a different electronic transition which is probably the triplet analogue of the singlet transition at 3867Å. Analysis of this triplet spectrum, which displays no immediately recognisable features, has not yet been attempted.

### V. 2(b) The Singlet System

The main features of the 3867Å transition of acrolein are shown by the low resolution spectrum obtained with an automatic recording spectrometer. (fig. 15). A similar spectrum of acrolein - $d_1$ is also shown. (fig. 16). Microphotomer charts obtained from plates of moderate resolution are reproduced in figs. 17-20. The observed band frequencies and assignments for acrolein and acrolein - $d_1$ are given in tables 7 and 8.

In both molecules, the spectra are composed of series of sharp bands extending to the violet from about 3860Å and superimposed on a continuum which has an intensity maximum at about 3,300Å. The band systems become more diffuse to shorter wavelengths and virtually all trace of structure has disappeared at 3,200Å. This, together with the absence of J-structure in the high resolution spectra, shows that the continuum is a result of predissociation. In contrast, the analogous propynal molecule, which has similar moments of inertia, gives rise to a spectrum having well defined J-structure.

The most prominent feature of the acrolein spectrum is undoubtedly the progression in the upper state carbonyl stretching frequency with the value of 1265 cm.$^{-1}$. Each member of this progression is accompanied by a strong band 490 cm.$^{-1}$ to the violet and, after the first member, both the carbonyl band and the satellite appear to be double. In addition to these strong bands, there are a large number of much weaker bands which, although noted by Eastwood and Snow, were not studied by them. There at first appears, then, three prominent intervals 490, 1265 and 1410 cm.$^{-1}$ with which combine successive upper state carbonyl quanta. These three are labelled B, A and C respectively, the superscript number denoting the number of associated carbonyl quanta and the subscript number the number of associated torsional quanta in sequences. The A, B and C progressions are easily the most intense and important in the spectrum and set the general pattern of the band system.

Inspection of the spectrum under moderate resolution reveals a dichotomy in the band structures which is to some extent reflected in the difference in intensities between the bands of the A, B and C progressions and the others. The bands of the main progressions outlined above are all characterised by the presence of well developed K-structure, consisting of a series of 15 or more lines degrading slightly to the violet. See fig. 19. The major part of the band intensity is, however, concentrated in the smooth contoured peak immediately to the red of the fine structure. The lower intensity bands, in contrast, show no trace of fine structure and possess very sharp heads to the violet. There are, however, a number of weak bands which are not of this type and correspond in structure to the bands of the A, B and C progressions.

It is obvious that two different band types are present and these can be readily identified as perpendicular or parallel according as the K-structure is resolved or not. (See section I.6). The perpendicular bands are denoted by capital letters and the parallel bands by small letters in our notation. In this case, the parallel bands can only be type A but the perpendicular bands may be type B or C. Neither of the two band types resemble the typical infrared band envelopes and apparently the moments of inertia change to such an extent on excitation that further classification by comparison with infrared bands is not possible. The distinction between the two types of perpendicular band is important as it also implies a distinction between symmetry species since the symmetry classification of the electronic origin, a band of this type, determines the symmetry species of the electronic upper state.

Exactly the same types of bands are found in the near ultraviolet spectrum of glyoxal and indeed the origins of the analogous glyoxal and acrolein systems have almost identical band envelopes. The parallel bands are rather sharper in glyoxal but display the same general characteristics. It was shown by both vibrational and rotational analysis that the origin and all other bands of the main progression were type C, thus establishing the electronic upper state species as $A_u$. The great similarity in the origins of the band systems of the two molecules is, in itself, a convincing argument in favour of the same type C assignment of the acrolein origin. It is, however, possible to establish this conclusion by vibrational analysis of the acrolein spectrum itself although the rotational structure is too diffuse to be similarly useful.

Hot Bands

There is little doubt that the band $A_0^0$ at 25861 cm.$^{-1}$ is the origin of the system. All other workers are agreed on this assignment, although there is some doubt as to the position of the band centre which we take as the central minimum (in common with Eastwood and Snow): Inuzuka has, however, selected the intensity maximum 10 cm.$^{-1}$ to the red. Apart from the previously discussed triplet system, some weak absorption bands are observed to the red of the singlet origin. This consists of the three perpendicular bands noted by Eastwood and Snow and a very prominent parallel band. The perpendicular band F , 0-565 can be assigned with reasonable certainty as 0-1 transition of the totally symmetric lower state C-C=O bending vibration $\nu''_{12}$ which in the infrared has the value 564 cm.$^{-1}$ The separation of one of the perpendicular bands, G , 0-312 is exactly twice that of the parallel band $a_0^0$ which, at the very low value of 157 cm.$^{-1}$, strongly suggests the ground state carbon-carbon single bond torsional vibration $\nu''_{18}$. As this vibration is non-totally symmetric, transitions from successive lower state quanta to the vibrationless upper state level should give rise to an alternation in band types due to the alternating symmetry species of the lower state levels. This is exactly what is observed, the 0-2 transition being perpendicular, the 0-1 parallel and the 0-0 again perpendicular, assuming that the perpendicular bands are type C. This assumption is necessary if the assignment is correct, as the successive bands must have different symmetries. The assignment of the 157 cm.$^{-1}$ interval to $\nu''_{18}$ therefore establishes the origin as type C and hence the electronic upper state as $A''$. It is important in view of the consequences of this assignment to confirm it as far as possible. Fortunately, the frequencies of the torsional vibrations of both acrolein and acrolein - $d_1$ could be calculated by applying the method of Pitzer to the thermodynamic data for the cis-trans interconversion.

Assuming the normal cosine barrier the potential energy of rotation is given by the expression:

$$V = \tfrac{1}{2}V_1 (1 - \cos\phi) + \tfrac{1}{2}V_2 (1 - \cos 2\phi) \qquad (1)$$

where $V_1$ and $V_2$ are defined as in fig. 6.

Since the twisting moment constant

$$k = \frac{d^2V}{d\phi^2}$$

we have

$$k = \frac{d^2V}{d\phi^2} = \tfrac{1}{2}V_1 \cos\phi + 2V_2 \cos 2\phi \qquad (2)$$

for the trans form $\phi = 0$ so that

$$k \text{ trans} = \left(\frac{d^2V}{d\phi^2}\right)_{\phi=0} = \tfrac{1}{2}V_1 + 2V_2 \qquad (3)$$

The potential function has maxima or minima when

$$\frac{dV}{d\phi} = 0$$

that is, for values of $\phi$ given by the equation

$$\tfrac{1}{2}V_1 \sin\phi_m + 2V_2 \sin\phi_m \cos\phi_m = 0 \qquad (4)$$

Evidently $\sin \phi_m = 0$ or 1, and therefore

$$\cos \phi_m = \frac{V_1}{4V_2}$$

Substituting $\frac{V_1}{4V_2}$ for $\cos \phi$ in (1) we have:

$$V_m = \frac{V_1^2 + 8V_1V_2 + 16V_1^2}{16\ V_2}$$

Introducing the values $V_1 = 2.06$ and $V_m = 7.02$ k. cal/mole (51) we find

$$V_2 = 5.94 \text{ k. cal/mole}$$

and substituting the values for $V_1$ and $V_2$ in (3) we have

$$k_{trans} = 12.921 \text{ k. cal/mole.}$$

Now $k = 4\pi^2 c^2 \sigma^2 I_m$ where $I_m$ is the reduced moment of inertia of the $m^{th}$ top, in this case -CHO. $I_m$ was found, using Pitzer's method, to be $9.189 \times 10^{-40}$ g. cm$^2$ and hence

$$\sigma = 166 \text{ cm.}^{-1}.$$

Considering the very simple expression used for the potential curve, the agreement is very good and certainly supports the $\nu''_{18}$ assignment. Furthermore, the same assignment also serves to interpret many of the details of the band structures to the violet of the origin.

Upper state Vibrations

Since the origin is a type C band, all the parallel type A bands must be associated with non-totally symmetric vibrations, while the other perpendicular bands are obviously attributable to totally symmetric vibrations and to sequences and even-numbered quantum changes of non-totally symmetric vibrations. The first parallel band to the violet of the origin, $b^o_o$, 0 + 252, must of course be due to a non-totally symmetric vibration. If it is assigned to the 1-0 torsional transition giving a value of 252 cm.$^{-1}$ for $\nu'_{18}$, the 1-1 sequence should then, being totally symmetrical occur as a perpendicular band 95 cm.$^{-1}$ above the origin. The presence of $A_1^0$, 0 + 93 cm.$^{-1}$ with the required band envelope and position confirms this assignment and strengthens the case for the suggested assignment of both $\nu''_{18}$ and $\nu'_{18}$. Fig. 7. shows the relationships of the various bands and energy levels associated with the torsional vibration in this region of the spectum.

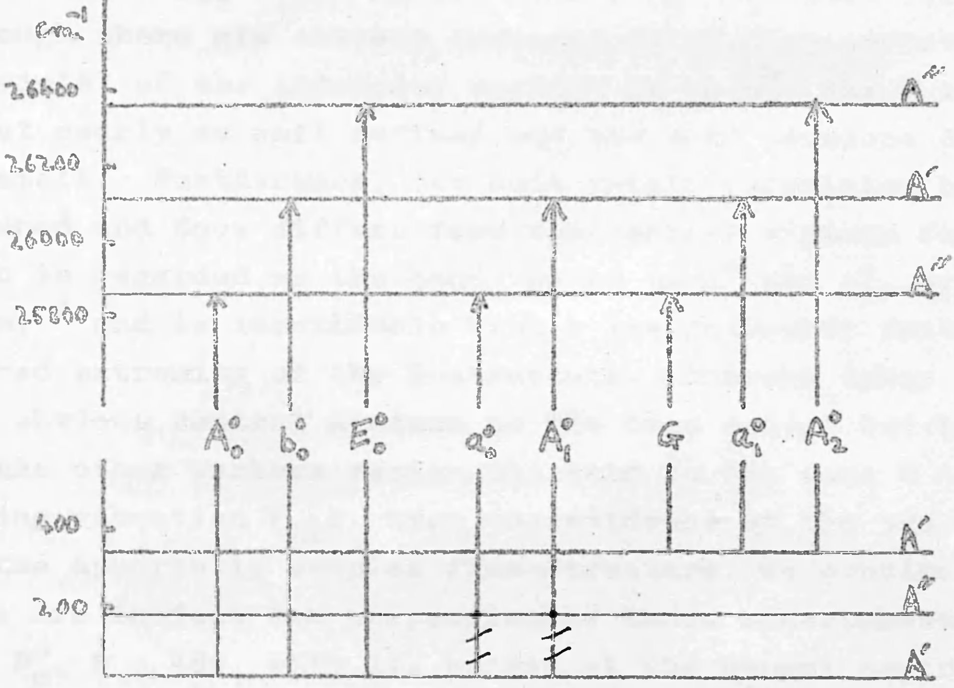


Fig. 7.

Moving further to the violet, two other parallel bands are observed before the next strong perpendicular band $B_0^0$. The first of these $c_0^0$, 0 + 333, cannot be accounted for by any combination of the torsional frequencies and is therefore assigned to an upper state fundamental. Of the remaining non-totally symmetric vibrations, that of lowest frequency is the carbon-carbon double bond torsional vibration $\nu'_{17}$ which therefore seems the most appropriate. The decrease in frequency in comparison with the lower state value of 588 cm.$^{-1}$ is considerable but is a natural consequence of the increase in the single bond torsional frequency on excitation. The other parallel band $c^{o}_{1}$ may then be assigned to the $\nu_{18}$ torsional sequence on $c^{o}_{o}$. The weak perpendicular band, $A^{o}_{2}$, is the second $\nu_{18}$ torsional sequence on the origin $A^{o}_{o}$.

The strong perpendicular band at about 500 cm$^{-1}$ from the origin appears, at first sight, to be very similar to the other strong bands of this type, $A^{o}_{o}$, $A^{o}_{1}$, etc. However, although there are obvious indications of fine structure to the violet of the intensity maximum as in $A^{o}_{o}$, the K-structure is not nearly so well defined and the band envelope differs in detail. Furthermore, the band origin calculated by Eastwood and Snow differs from the central minimum feature, which is regarded as the band centre in $A^{o}_{o}$ and $A^{o}_{1}$, by about 20 cm.$^{-1}$ and is identifiable with a low intensity feature at the red extremity of the K-structure. Inuzuka takes the more obvious central minimum as the band centre but both he and the other workers assign the band to the same C - C = O bending vibration $\nu_{12}$. From the evidence of the two origins and the apparently complex fine-structure, we conclude that there are in fact two perpendicular bands superimposed. The band $B^{o}_{o}$, 0 + 489, with its origin at the normal central minimum position, can then be assigned to $\nu'_{12}$ while the weaker band $E^{o}_{o}$, 0 + 508, with its origin at the calculated position can be assigned to the totally symmetric 2 - 0 transition of $\nu'_{18}$. The $\nu_{18}$ torsional sequences $B^{o}_{1}$ and $B^{o}_{2}$ do not fit well with the known values of $\nu''_{18}$ and $\nu'_{18}$ and neither can these bands be considered as possible sequences on $E^{o}_{o}$. Due to the general similarity of $B^{o}_{1}$, $B^{o}_{2}$ and $B^{o}_{o}$ with $A^{o}_{1}$, $A^{o}_{2}$ and $A^{o}_{o}$ it seems almost certain that the torsional sequence interpretation is correct and it may be that the discrepancies are due to Fermi resonance involving $B^{o}_{o}$ and $B^{o}_{1}$.

To the violet of $B\cancel{A}_2^0$, a number of parallel bands occur and superficially it appears as if these bands are analogous to $b_0^0$, $c_0^0$ and $c_1^0$ with $B_0^0$ as the origin. Measurements show that this interpretation is incorrect and the weak parallel bands d - h present a difficult problem as they do not appear to arise from any plausible combination of frequencies and the number of non-totally symmetric fundamentals is insufficient to account for all the bands. It is almost certain that the vinyl twisting and wagging vibrations, $\nu'_{14}$ and $\nu'_{15}$, are active but cannot be assigned with certainty to any specific bands in this region. All the features so far discussed have been common to the spectra of both acrolein and acrolein - $d_1$ but the weak perpendicular band $D_0^0$, 0 + 1133, is not observed in the spectrum of the deuterated molecule. $D_0^0$ may therefore be assigned to the upper state formyl hydrogen in-plane rocking vibration $\nu'_8$ as the ground state frequency, 1361 cm.$^{-1}$, drops considerably on deuteration to around 1040 cm.$^{-1}$. Presumably in the normal molecule the close association with $\nu'_5$ makes $\nu'_8$ active though weak. This situation does not, of course, obtain in the deuterated molecule and hence the band $D_0^0$ is absent.

The strong perpendicular band $A_0^1$, 0 + 1266, is the second member of the carbonyl progression and the band structure immediately to the violet of the first member $A_0^0$ is here repeated. The sequences $A_1^1$ and $A_2^1$ are obscured by the intense band $C_0^0$, 0 + 1410, which is assigned to the carbon - carbon stretching vibration $\nu'_6$. The decrease in frequency on excitation is consistent with the redistribution of bond order implied by the corresponding changes in the torsional vibrations. For the normal molecule, the sequence $A_1^1$ can just be discerned as a shoulder on $C_0^0$. The parallel bands $b_0^1$, $c_0^1$ and $c_1^1$ correspond to $b_0^0$, $c_0^0$ and $c_1^0$ with the addition of one quantum of $\nu'_5$. A puzzling feature is the apparent doubling of these bands to form pairs with a separation of about 30 cm.$^{-1}$. This cannot be due to the superposition of the b and c frequencies on the $C_0^0$ band as the $A_0^1 - C_0^0$ separation is 150 cm.$^{-1}$. Unfortunately, the situation, particularly with regard to such weak bands, is unfavourable in this region which is at the high frequency limit of the glass optical system of the spectrograph. The frequencies of the excited state fundamentals are listed in table 4 with the appropriate ground state values.

Table 4.

Excited State Fundamentals

All values are in cm.$^{-1}$

| Species | Fundamental | Ground State | | Excited State | |
|---|---|---|---|---|---|
| | | $CH_2$=CH-CHO | $CH_2$=CH-CDO | $CH_2$=CH-CHO | $CH_2$=CH-CDO |
| a′ | $\nu_5$ | 1723 | 1709 | 1266 | 1274 |
| | $\nu_6$ | 1626 | 1620 | 1410 | 1394 |
| | $\nu_8$ | 1361 | 1040 | 1133 | - |
| | $\nu_{12}$ | 564 | 562 | 489 | 481 |
| a″ | $\nu_{17}$ | 589 | 556 | 333 | 328 |
| | $\nu_{18}$ | 157 | 150 | 251 | 243 |

## V.3. The Nature of the Transition

As we have already seen, the assignment of the non-totally symmetric $\nu_{18}$ fundamental to certain of the parallel bands shows that the origin of the system is type C and the electronic excited state therefore has $A''$ symmetry. The main band system, composed of similar type C bands, is therefore allowed by the symmetry selection rules. It has been shown that, in addition, there are a large number of weak parallel bands, necessarily of type A, which must be associated with non-totally symmetric vibrations. It follows that these bands form a forbidden component of the spectrum and, to account for their appearance, it must be supposed that this component is the result of vibronic interaction involving some other electronic state which must therefore possess $A'$ symmetry. Presumably this is the upper state of the lowest $\pi^* - \pi$ transition.

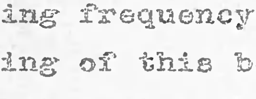
## V.4 Structure of the Excited State

Apart from the carbonyl stretching vibration, no fundamental is active for changes of more than two upper state quanta and, although the $\nu'_{18}$ torsional vibration is slightly anharmonic, the second quantum being about 7 cm.$^{-1}$ greater than the first, it is clear that the molecule is planar in the excited state.

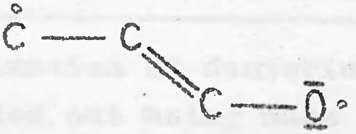
The carbonyl progression extends over a number of quanta and the intensity maximum is displaced from the origin. This evidence, with the substantial decrease in the carbonyl stretching frequency on excitation, is indicative of some lengthening of this bond, probably of the order of 0.1Å. It is probable that this is the only major change in structure, although the excited state values for the $\nu'_{17}$ and $\nu'_{18}$ torsional vibrations indicate small changes in the carbon - carbon bond lengths.

## V.5. Electronic Structure of the Excited State

In the simplest example of $\pi^* - n$ transitions, the ${}^1A_2 - {}^1A_1$ transition of formaldehyde, the energies of the $\pi_{co}$ and $\pi^*_{co}$ orbitals are similar and their bonding and antibonding properties are diminished, resulting in what is effectively a three electron bond



In acrolein, however, the presence of the carbon - carbon double bond affords the possibility of conjugative electron displacement which could result in a contribution to the excited state electronic structure from the canonical form represented by:



In the excited state of acrolein we have shown that the single bond torsional vibration $\nu_{18}$ is 60% greater in frequency that in the ground state while the double bond torsional vibration $\nu_{17}$ similarly decreases by 43%. These significant changes must be the result of an increase in bond order in the single bond and a corresponding decrease in the double bond, indicating that conjugative displacements of the type suggested do take place to a considerable extent. We conclude, then, that, in the excited state, the two predominant electronic structures can be represented by:

This diradical structure of the excited state has been found to exist in the analogous propynal molecule, the excited state of which may be represented by the structures:

It appears that the formation of diradical structures on excitation may well be general in $\alpha,\beta$-unsaturated carbonyl compounds. This behaviour could provide a new basis for the interpretation of the reaction mechanisms of the complex photochemical rearrangements exhibited by many molecules of this particular type and indeed some work has already been done in this direction.[73,74]

# VI. APPENDIX

## VI. 1. Determination of Deuterium in Acrolein - $d_3$

At first, the estimation of deuterium in the acrolein - $d_3$ samples was carried out using mass spectroscopic techniques and the results were obtained in the form of a set of five equations in four variables, corresponding to the four isotopes n, $d_1$, $d_2$ and $d_3$. A least squares treatment was applied to these equations. Each variable was selected in turn and the coefficients of all the variables multiplied by that of the selected variable. The five new equations were then summed, yielding one equation for each variable. These four simultaneous equations were then solved using the LEO I programme with an English Electric DEUCE computor. This procedure gives no indication of the position of deuterium substitution in the molecule and nuclear magnetic resonance spectroscopy was employed to remedy this deficiency.

A known quantity ofthe hydrogen contaminated acrolein - $d_3$ was distilled into an N.M.R. sample tube, a known quantity of dioxan added and carbon tetrachloride was added to make up the required volume. The N.M.R. spectrum was obtained and the areas under the bands corresponding to the vinyl acrolein and dioxan protons evaluated. The known relative quantities and numbers of protons for the two molecules then enabled the proportion of deuterium in the vinyl group to be calculated. Test determinations with normal acrolein samples indicated that the method was not accurate and the difficulty of assignment of the bands made this method of estimation unreliable. In order to overcome the difficulties of assignment caused by the extensive interaction of the protons, it was decided to brominate the double bond and in this way reduce the complexity of the spectrum. 1;2-Dibromopropionaldehyde gives rise to a typical ABX spectrum, except that the four major lines of the X portion are split by coupling with the formyl proton. See fig. 21 (a). It was found that the dibromo derivative of the acrolein - $d_3$ sample showed no splitting of the lines of the X portion which can only mean that there is little hydrogen present in the formyl position. See fig. 21 (b). This is confirmed by the fact that the formyl proton peak, which, in the authentic 1;2-dibromopropionaldehyde spectrum, occurs at 0.58 τ , is entirely absent from the spectrum of the deuterated molecule.

## VI. 2. Mechanism of Deuteride Reduction

The presence of a substantial proportion of deuterium in the formyl position indicates that the source of the hydrogen impurity was actually the hydrogens of the hydroxyl methylene group in the propargyl alcohol. This conclusion is supported by the elaborate precautions taken to eliminate all other sources of hydrogen whether intra- or extra- molecular. From the information accumulated by the mass spectroscopic and N.M.R. determinations, it appears probable that all three carbon atoms of the deuterated allyl alcohol carried equal proportions of deuterium. (The deuterium proportion at the formyl position of the aldehyde is selectively enhanced by the oxidation process). To account for this phenomenon, it seems necessary to postulate the existence, during the reduction of the propargyl alcohol or acetate, of the cyclopropene anion in which all the carbon atoms are equivalent due to mesomeric shifts of the double bond.

## VI. 3 Infrared Spectra

### Table 5

### Vapour Infrared Spectra of Acrolein $CH_2 = CH - CHO$

All frequencies are in cm.$^{-1}$. Intensities are given as the apparent molecular extinction coefficient. The fundamentals and the corresponding symbols are listed in table 3 p.71

| | cm.$^{-1}$ | cm.$^{-1}$ | Intensity | Assignment |
|---|---|---|---|---|
| R | 3431.2 | 3431.2 | 4.3 | $2\nu_5 = 3445.4$ |
| P | 3415.1 | 3419.9 | | |
| R | 3359.2 | 3355.3 | | |
| Q | 3347.2 | 3347.5 | 0.3 | $\nu_6 + \nu_5 = 3348.4$ |
| P | 3338.5 | 3336.9 | | |
| R | 3252.1 | 3251.8 | | |
| Q | 3244.4 | 3244.6 | 0.3 | $2\nu_6 = 3251.4$ |
| P | 3234.7 | 3240.2 | | |
| R | 3113.0 | 3111.0 | | |
| Q | 3104.4 | 3102.1 | 4.7 | $\nu_1$ |
| P | 3095.6 | 3092.3 | | |
| R | 3009.3 | 3007.5 | | |
| Q | 2999.6 | 3001.4 | 4.5 | $\nu_2$ |
| P | 2989.7 | 2989.2 | | |
| R | 2809.7 | 2809.6 | | |
| min$^{m}$ | 2799.8 | 2800.1 | 21.4 | $\nu_4$ |
| P | 2790.6 | 2790.4 | | |

| | | | | |
|---|---|---|---|---|
| R | 2764.4 | 2764.3 | | |
| min$^m$ | 2754.6 | 2753.9 | 18.2 | See text for discussion |
| P | 2747.2 | 2746.9 | | |
| R | 2703.6 | 2703.0 | | |
| min$^m$ | 2693.2 | 2693.1 | 13.1 | $2\nu_8 = 2722.4$ |
| P | 2686.8 | 2686.1 | | |
| R | 2052.5 | 2056.7 | | |
| Q | 2043.5 | 2049.8 | 1.6 | |
| P | 2036.8 | 2041.8 | | |
| R | 2003.8 | 2007.0 | | |
| P | 1997.2 | 1999.1 | 0.6 | |
| P | 1985.7 | 1988.0 | | |
| R | 1926.0 | 1926.3 | | |
| min$^m$ | 1917.0 | 1918.1 | 4.0 | $2\nu_{15} = 1918.4$ |
| P | 1910.6 | 1910.6 | | |
| R | 1831.5 | 1832.5 | | |
| min$^m$ | 1823.5 | 1825.2 | 4.1 | $2\nu_{11} = 1825.6$ |
| P | 1815.8 | 1816.6 | | |
| Rmax$^m$ | 1734.8 | 1732.6 | | |
| | 1726.0 | 1725.9 | | |
| min$^m$ | 1722.2 | 1723.1 | 214.0 | $\nu_5$ |
| | 1718.1 | 1719.3 | | |
| Pmax$^m$ | 1712.6 | 1713.0 | | |
| R | 1635.1 | 1635.4 | | |
| Q | 1625.8 | 1625.6 | 12.9 | $\nu_6$ |
| P | 1616.7 | 1616.3 | | |

| | | | | |
|---|---|---|---|---|
| R | 1488.0 | 1486.3 | | |
| $\min^{m}$ | 1480.5 | 1479.2 | 1.8 | $\nu_{11} + \nu_{12} = 1476.7$ |
| P | 1475.2 | 1473.3 | | |
| R | 1430.0 | 1429.5 | | |
| Q | 1422.5 | 1421.3 | 11.7 | $\nu_7$ |
| P | 1417.7 | 1412.8 | | |
| R | 1370.4 | 1369.7 | | |
| Q | 1361.5 | 1361.0 | 4.0 | $\nu_8$ |
| P | 1352.5 | 1351.7 | | |
| R | 1286.1 | 1285.0 | | |
| Q | 1276.5 | 1275.9 | 1.7 | $\nu_9$ |
| P | 1267.0 | 1266.0 | | |
| R | 1168.1 | 1166.6 | | |
| Q | 1160.0 | 1158.6 | 38.0 | $\nu_{10}$ |
| P | 1152.8 | 1149.0 | | |
| $\mathrm{Qmax}^{m}$ | 994.1 | 992.6 | | $\nu_{14}$ |
| $\mathrm{Qmax}^{m}$ | 959.6 | 958.8 | 48.3 | $\nu_{15}$ |
| R | 920.9 | 920.2 | | |
| $\min^{m}$ | 913.5 | 912.2 | 36.4 | $\nu_{11}$ |
| P | 906.1 | 904.4 | | |
| R | 743.5 | 743.5 | | |
| | 721.6 | 734.2 | 0.92 | $\nu_{12} + \nu_{18} = 720.9$ |
| P | 720.0 | 720.5 | | |

| | | | | |
|---|---|---|---|---|
| | 593.5 | 591.8 | 8.3 | $\nu_{17}$ |
| Qmax$^{m}$ | 589.7 | 587.8 | | |
| | 587.5 | 584.9 | | |
| R | 574.5 | 573.1 | | |
| Q | 564.5 | 563.4 | 6.6 | $\nu_{12}$ |
| P | 557.8 | 557.0 | | |

## Table 6

## Vapour Infrared Spectra of Acrolein - $d_1$ $CH_2 = CH - CDO$

| cm.$^{-1}$ | | Intensity | Assignment |
|---|---|---|---|
| R 3450.3 | | | |
| Q 3441.5 | (3431.7) | 0.85 | $2(2\nu_{11}) = 3492.2$ |
| P 3432.5 | | | |
| R 3399.9 | | | |
| Q 3391.3 | (3401.1) | 3.5 | $2\nu_5 = 3406.6$ |
| P 3382.8 | | | |
| R 3331.5 | | 0.21 | $\nu_5 + \nu_6 = 3323.8$ |
| P 3314.7 | | | |
| R 3247.2 | | 0.21 | $2\nu_6 = 3241.0$ |
| P 3229.5 | | | |
| R 3110.7 | | | |
| Q 3101.5 | | 4.4 | $\nu_1$ |
| P 3092.2 | | | |
| R 3080.7 | | | |
| Q 3069.2 | | 3.3 | impurity |
| P 3059.4 | | | |

| | | | |
|---|---|---|---|
| R | 3038.9 | | |
| Q | 3029.4 | 2.0 | impurity |
| P | 3018.4 | | |
| R | 2992.9 | | |
| | 2987.9 | 2.3 | $\nu_2$ |
| | 2984.2 | | |
| P | 2975.5 | | |
| R | 2809.6 | | |
| min$^m$ | 2797.8 | 1.4 | Almost certainly $\nu_4$ of normal acrolein due to small amount of formyl hydrogen remaining |
| P | 2792.4 | | |
| R | 2731.1 | | |
| min$^m$ | 2714.0 | 1.2 | Probably $2\nu_8$ of normal acrolein |
| P | 2705.1 | | |
| P | 2705.1 | | |
| | 2563.0 | 0.21 | |
| R | 2431.0 | | |
| Q | 2422.9 | 0.32 | $\nu_9 + \nu_{10} = 2427.9$ |
| P | 2413.4 | | |
| R | 2211.5 | | |
| min$^m$ | 2202.6 | 1.5 | |
| P | 2194.0 | | |
| R | 2117.1 | | |
| min$^m$ | 2110.2 (2090.8) | 18.3 | $2\nu_8$ |
| P | 2096.1 | | |

| | | | | |
|---|---|---|---|---|
| R | 2071.1 | | | |
| $\min^m$ | 2060.4 | (2079.8) | 28.7 | $\nu_4$ |
| P | 2051.8 | | | |
| R | 1927.5 | | | |
| Q | 1921.0 | | 3.0 | $2.\nu_{15} = 1918.4$ |
| P | 1910.5 | | | |
| R | 1847.5 | | | |
| Q | 1839.5 | | 0.24 | $\nu_{19} + \nu_{12} = 1837.0$ |
| P | 1829.5 | | | |
| R | 1760.5 | | | |
| Q | 1751.6 | (1746.1) | 27.0 | $2\nu_{11} = 1753.6$ |
| P | 1743.7 | | | |
| R | 1712.5 | | | |
| Q | 1703.3 | (1708.8) | 210.0 | $\nu_5$ |
| P | 1695.5 | | | |
| R | 1630.5 | | | |
| | 1626.5 | | | |
| | 1620.5 | | 3.0 | $\nu_6$ |
| | 1615.9 | | | |
| | 1607.8 | | | |
| R | 1412.3 | | | |
| Q | 1403.3 | | 13.9 | $\nu_7$ |
| P | 1394.3 | | | |
| R | 1283.3 | | | |
| Q | 1275.2 | | 3.0 | $\nu_9$ |
| P | 1265.4 | | | |

| | | | |
|---|---|---|---|
| R | 1161.0 | | |
| Q | 1152.7 | 29.7 | $\nu_{10}$ |
| P | 1143.9 | | |
| $Q\max^{m}$ | 992.6 | 23.3 | $\nu_{14}$ |
| $Q\max^{m}$ | 959.2 | 43.1 | $\nu_{15}$ |
| R | 884.6 | | |
| Q | 876.8 | 14.3 | $\nu_{11}$ |
| P | 867.0 | | |
| Q | 846.3 | 4.0 | $\nu_{16}$ |
| P | 837.1 | | |
| | 692.5 | weak | |
| R | 567.9 | | |
| Q | 561.8 | 4.1 | $\nu_{12}$ |
| $Q\max^{m}$ | 555.7 | 7.1 | $\nu_{17}$ |

## Table 7

## The Near Ultraviolet Spectrum of Acrolein

The frequencies given for the perpendicular bands generally refer to the central minimum except where otherwise stated in the text. See fig. 19. In the case of the parallel bands, the frequencies are those of the sharp band heads to the violet. The intensities are estimated from the low resolution spectra and are expressed by an arbitrary scale, 0 - 10, in which the strongest band, $C_o^o$ has the value 10. The origin of the acrolein system appears to be slightly more intense than that of the acrolein - $d_1$ System.

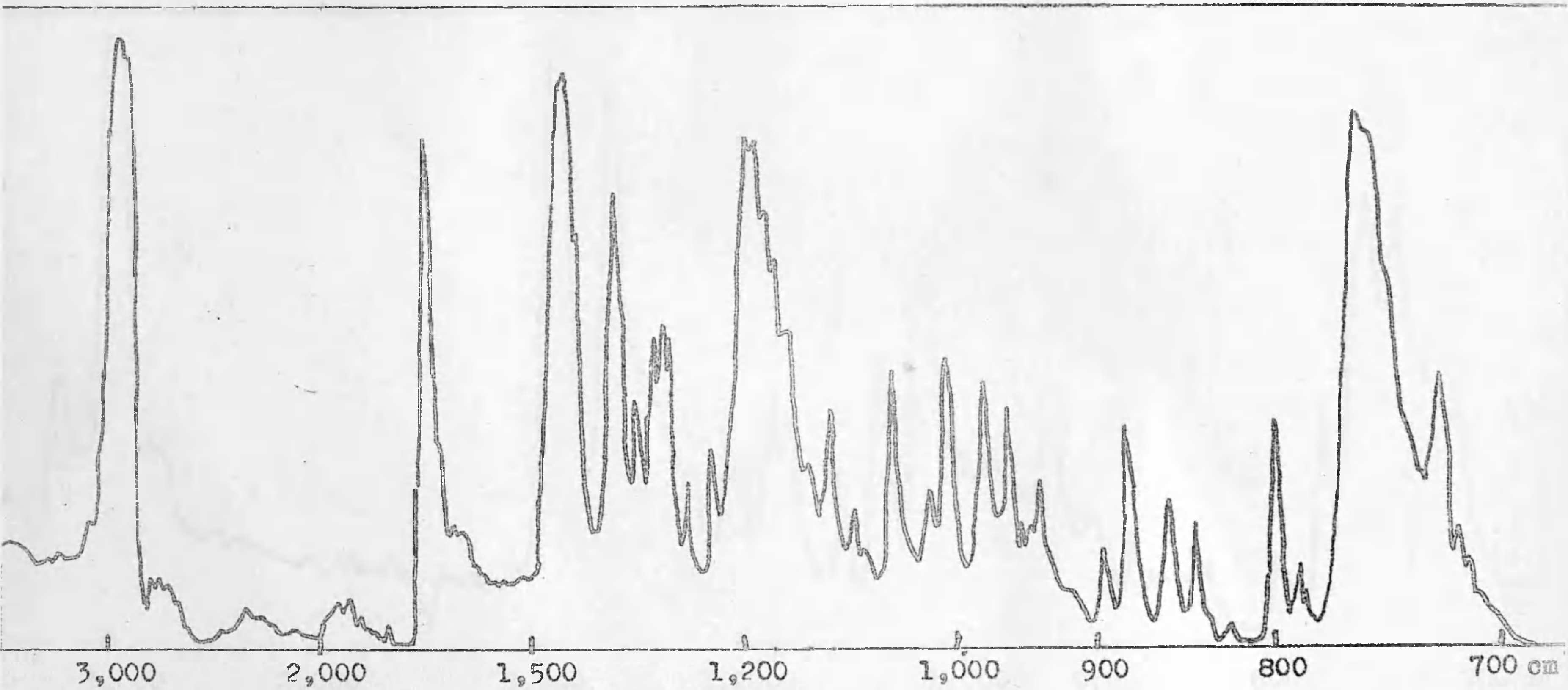
| Frequency cm.$^{-1}$ | Separation from origin | Intensity | Notation | Assignment |
|---|---|---|---|---|
| 25296.5 | -564.9 | vw | F | $\nu_o - \nu''_{12}$ |
| 25549.4 | -312.0 | vw | G | $\nu_o - 2\nu''_{18}$ |
| 25644.6 | -216.8 | vw | H | |
| 25705.2 | -156.2 | vw | $a_o^o$ | $\nu_o - \nu''_{18}$ |
| 25792.1 | -69.3 | vw | | $\nu_o + \nu'_{18} - 2\nu''_{18}$ |
| 25861.4 | 0.0 | 8.8 | $A_o^o$ | $\nu_o$ |
| 25953.8 | 92.4 | 4.0 | $A_1^o$ | $\nu_o + (\nu'_{18} - \nu''_{18})$ |
| 25980.7 | 119.3 | vw | | |
| 26055.6 | 194.2 | 0.9 | $A_2^o$ | $\nu_o + 2(\nu'_{18} - \nu''_{18})$ |
| 26079.5 | 228.1 | vw | | |
| 26112.5 | 251.1 | 1.1 | $b_o^o$ | $\nu_o + \nu'_{18}$ |
| 26159.9 | 298.5 | vw | | |
| 26194.0 | 332.6 | 1.4 | $c_o^o$ | $\nu_o + \nu'_{17}$ |
| 26278.2 | 416.8 | 0.6 | $c_1^o$ | $\nu_o + \nu'_{17} + (\nu'_{18} - \nu''_{18})$ |
| 26350.2 | 488.8 | 5.4 | $B_o^o$ | $\nu_o + \nu'_{12}$ |
| 26369.3 | 507.9 | 2.2 | $E_o^o$ | $\nu_o + 2\nu''_{18}$ |
| 26432.4 | 571.0 | 2.2 | $B_1^o$ | $\nu_o + \nu'_{12} + (\nu'_{18} - \nu''_{18})$ |
| 26513.0 | 651.6 | 0.6 | $B_2^o$ | $\nu_o + \nu'_{12} + 2(\nu'_{18} - \nu''_{18})$ |
| 26592.3 | 730.9 | 0.9 | $d_o^o$ | |

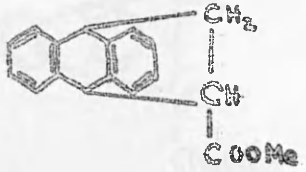
| Frequency cm.$^{-1}$ | Separation from origin | Intensity | Notation | Assignment |
|---|---|---|---|---|
| 26669.8 | 808.4 | 0.9 | $e_o^o$ | |
| 26747.3 | 885.9 | 1.1 | $f_o^o$ | |
| 26770.5 | 909.1 | 1.1 | $g_o^o$ | |
| 26819.2 | 957.8 | 1.7 | $h_o^o$ | |
| 26994.0 | 1132.6 | 2.5 | $D_o^o$ | $\nu_o + \nu'_8$ |
| 27122.0 | 1260.6 | 9.0 | $A_o^1$ | $\nu_o + \nu'_5$ |
| 27210.6 | 1349.2 | 6.8 | $A_1^1$ | $\nu_o + \nu'_5 + (\nu'_{18} - \nu''_{18})$ |
| 27271.6 | 1410.2 | 10.0 | $C_o^o$ | $\nu_o + \nu'_6$ |
| 27372.6 | 1511.2 | 2.2 | $b_o^1$ | $\nu_o + \nu'_5 + \nu'_{18}$ |
| 27403.9 | 1542.5 | | | |
| 27449.7 | 1588.3 | 2.2 | $c_o^1$ | $\nu_o + \nu'_5 + \nu'_{17}$ |
| 27484.0 | 1622.6 | | | |
| 27520.1 | 1658.7 | 1.5 | $c_1^1$ | $\nu_o + \nu'_5 + \nu'_{17} + (\nu'_{18} - \nu''_{18})$ |

Table 8

## The Near Ultraviolet Spectrum of Acrolein - $d_1$

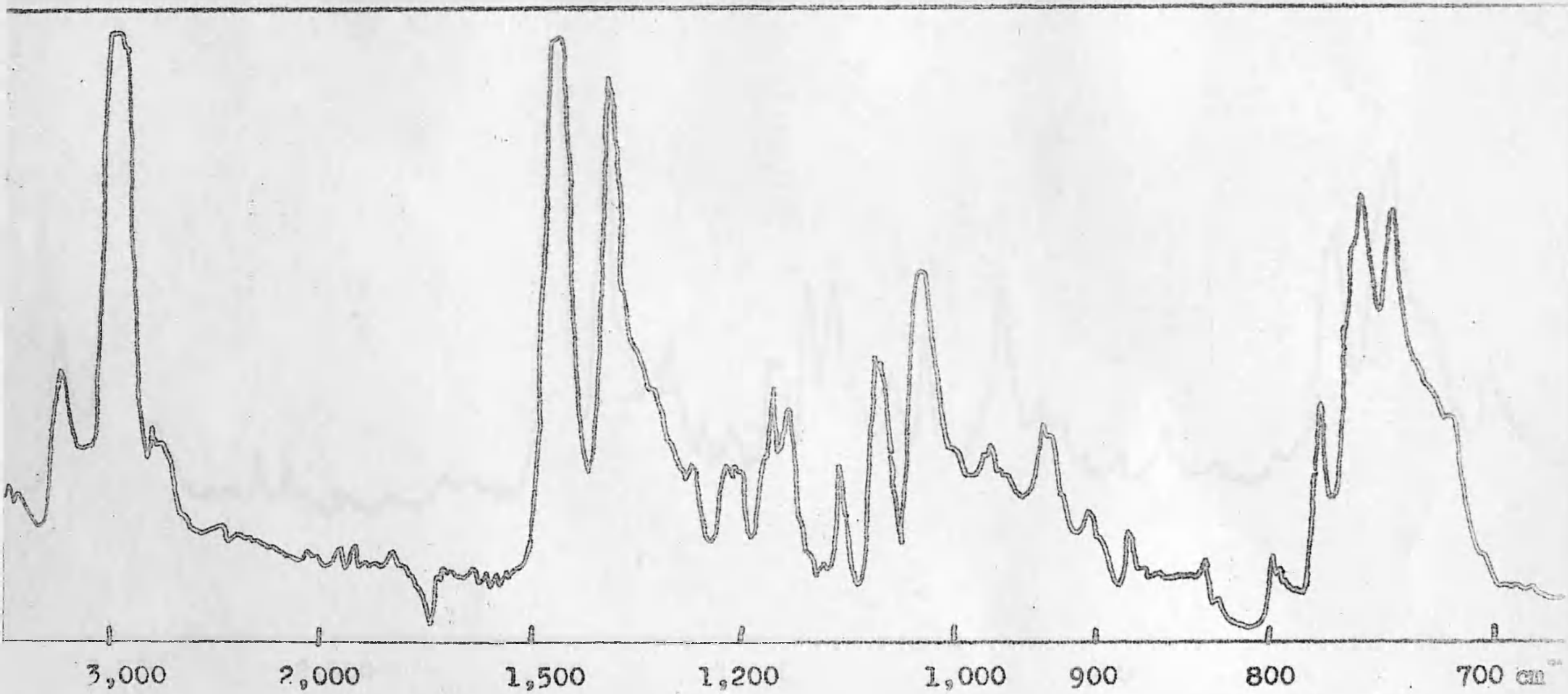
| Frequency cm.$^{-1}$ | Separation from origin | Intensity | Notation | Assignment |
|---|---|---|---|---|
| 25321.2 | -570.2 | vw | F | |
| 25588.1 | -303.3 | vw | G | $\nu_0 - 2\nu''_{18}$ |
| 25740.6 | -150.8 | vw | $a_0^0$ | $\nu_0 - \nu'_{18}$ |
| 25891.4 | 0.0 | 7.1 | $A_0^0$ | $\nu_0$ |
| 25986.5 | 95.1 | 3.8 | $A_1^0$ | $\nu_0 + (\nu'_{18} - \nu''_{18})$ |
| 26076.9 | 185.5 | vw | $A_2^0$ | $\nu_0 + 2(\nu'_{18} - \nu''_{18})$ |
| 26107.0 | 215.6 | vw | | |
| 26134.8 | 243.4 | 1.0 | $b_0^0$ | $\nu_0 + \nu'_{18}$ |
| 26167.5 | 276.1 | vw | | |
| 26192.5 | 301.1 | vw | | |
| 26219.1 | 327.7 | 1.1 | $c_0^0$ | $\nu_0 + \nu'_{17}$ |
| 26279.0 | 387.6 | vw | | |
| 26306.1 | 414.7 | 1.0 | $c_1^0$ | $\nu_0 + \nu'_{17} + (\nu'_{18} - \nu''_{18})$ |
| 26372.5 | 481.1 | 4.0 | $B^0{}_0$ | $\nu_0 + \nu'_{12}$ |
| 26387.0 | 495.6 | 1.9 | $E_0^0$ | $\nu_0 + 2\nu'_{18}$ |
| 26458.0 | 566.6 | 1.9 | $B_1^0$ | $\nu_0 + \nu'_{12} + (\nu'_{18} - \nu''_{18})$ |
| 26545.4 | 654.0 | vw | $B_2^0$ | $\nu_0 + \nu'_{12} + 2(\nu'_{18} - \nu''_{18})$ |
| 26601.6 | 710.2 | 0.7 | $d_0^0$ | |
| 26688.5 | 797.1 | 0.7 | $e_0^0$ | |
| 26768.5 | 877.1 | 1.1 | $f_0^0$ | |
| 26790.2 | 898.8 | 1.1 | $g_0^0$ | |
| 26846.2 | 954.8 | 1.7 | $h_0^0$ | |
| 27165.2 | 1273.8 | 10.0 | $A_0^1$ | $\nu_0 + \nu'_5$ |
| 27285.9 | 1394.5 | 10.0 | $C_0^0$ | $\nu_0 + \nu'_6$ |
| 27403.8 | 1512.4 | 2.6 | $b_0^1$ | $\nu_0 + \nu'_5 + \nu'_{18}$ |
| 27488.6 | 1597.2 | 2.2 | $c_0^1$ | $\nu_0 + \nu'_5 + \nu'_{17}$ |
| 27573.8 | 1682.4 | 2.6 | $c_1^1$ | $\nu_0 + \nu'_5 + \nu'_{17} + (\nu'_{18} - \nu''_{18})$ |
| 27633.7 | 1742.3 | 5.0 | $B_0^1$ | $\nu_0 + \nu'_5 + \nu'_{12}$ |
| 27729.0 | 1838.6 | 3.1 | $B_1^1$ | $\nu_0 + \nu'_5 + \nu'_{12} + (\nu'_{18} - \nu''_{18})$ |





Methyl 9; 10-Ethanoanthracene-11-Carboxylate
(Nujol Mull)

Fig. 8.



9; 10 - Ethanoanthracene-11-Methanol

(Nujol Mull)

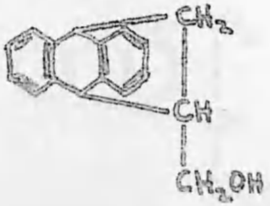
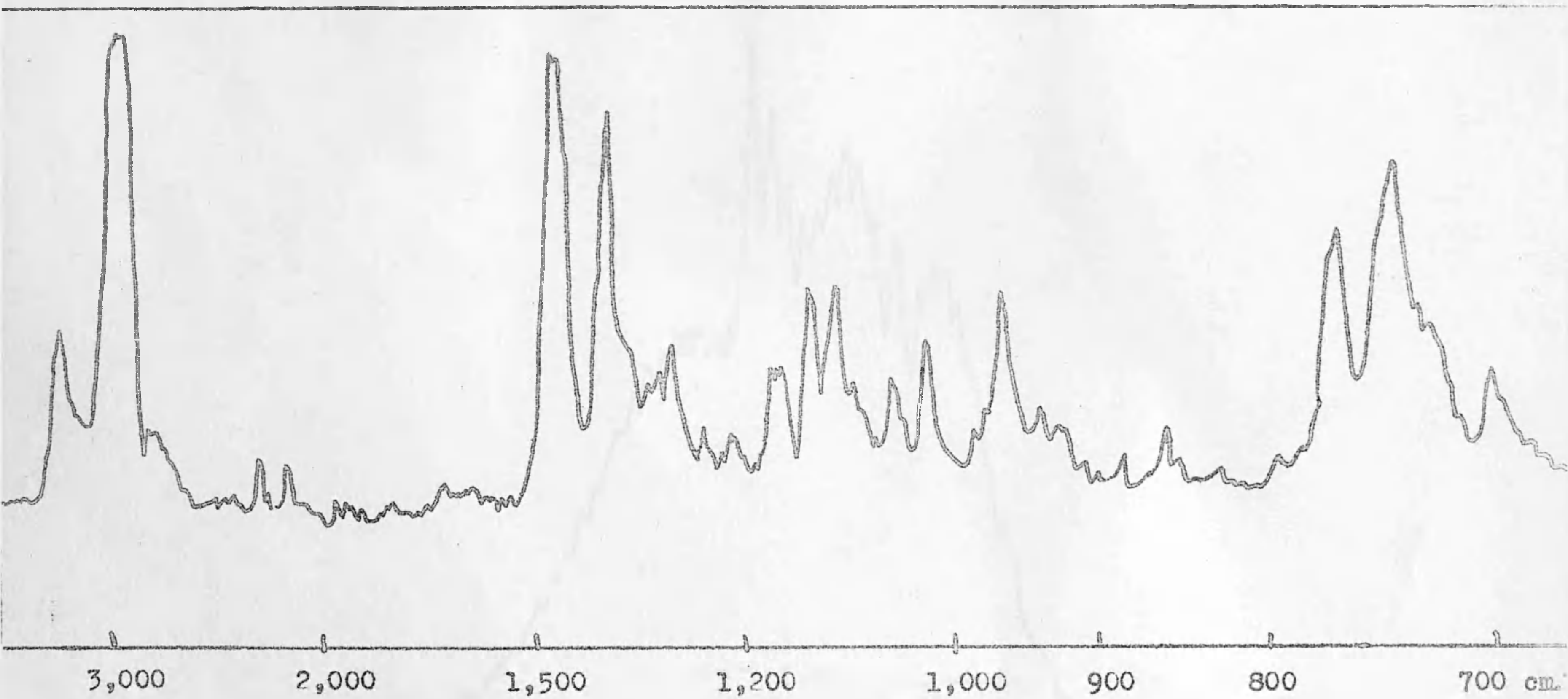
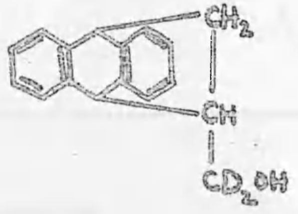


Fig. 9.

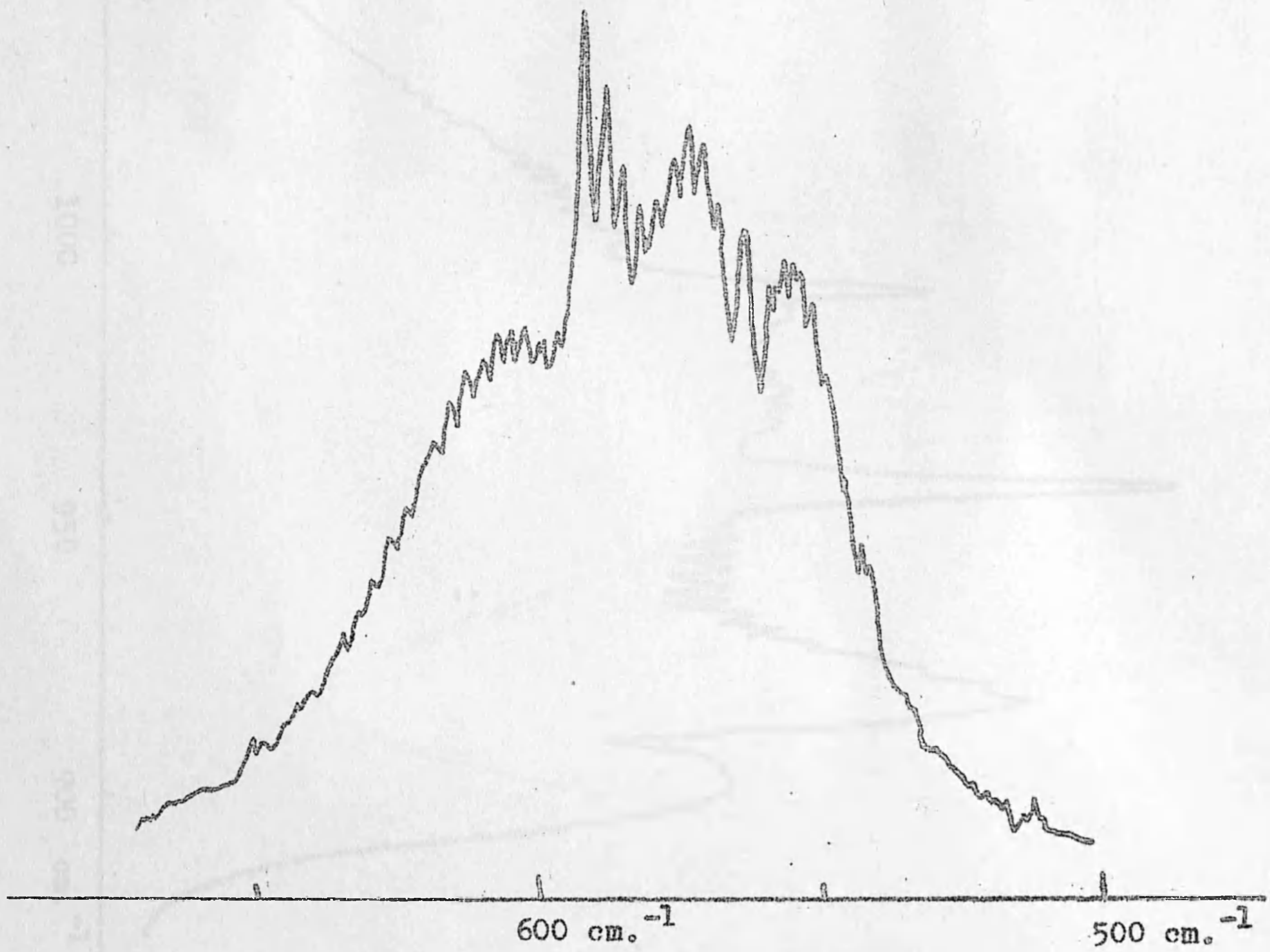




9, 10-Ethanoanthracene-11-Methanol-13-$d_2$

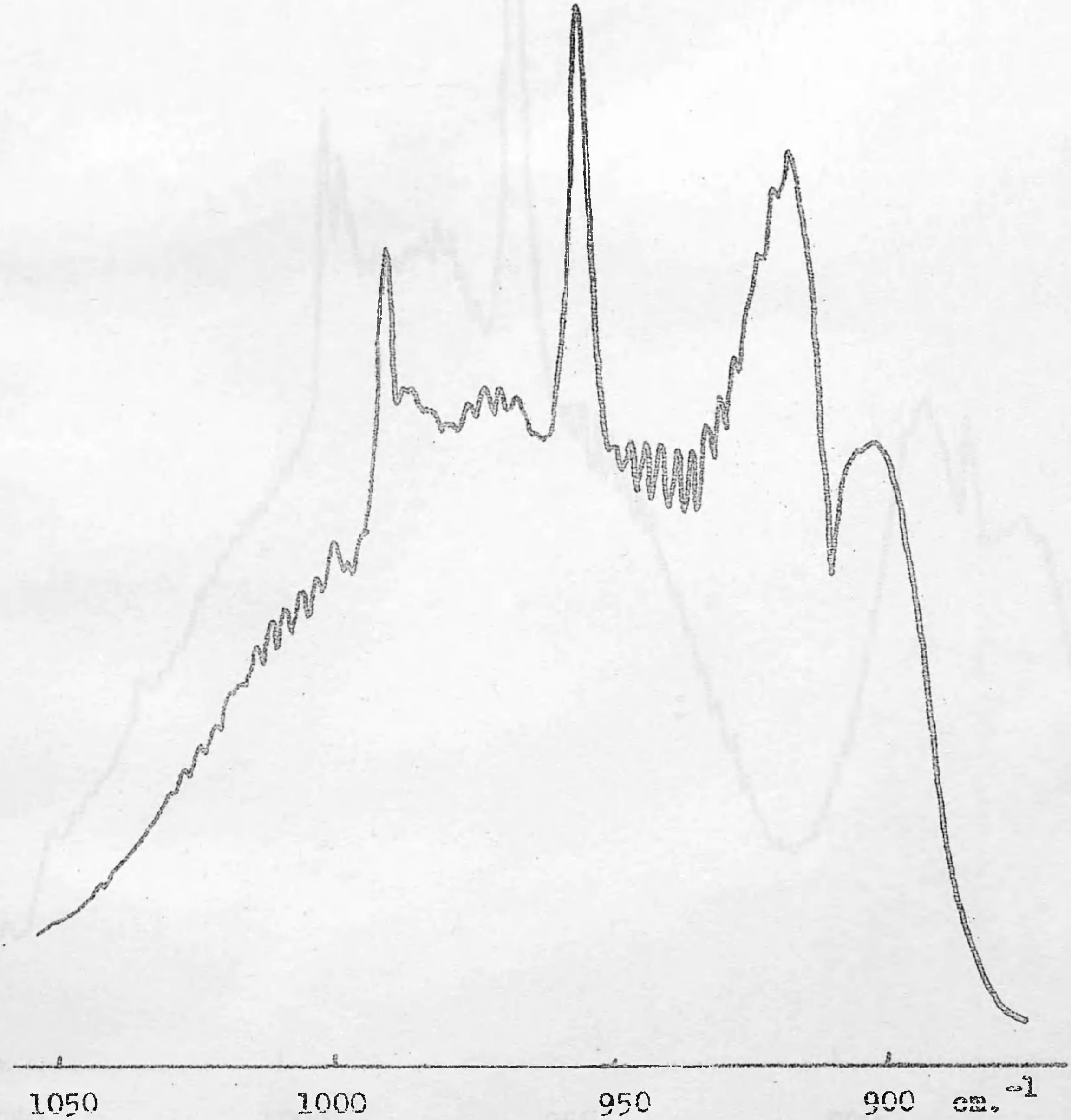
(Nujol Mull)

Fig. 10.



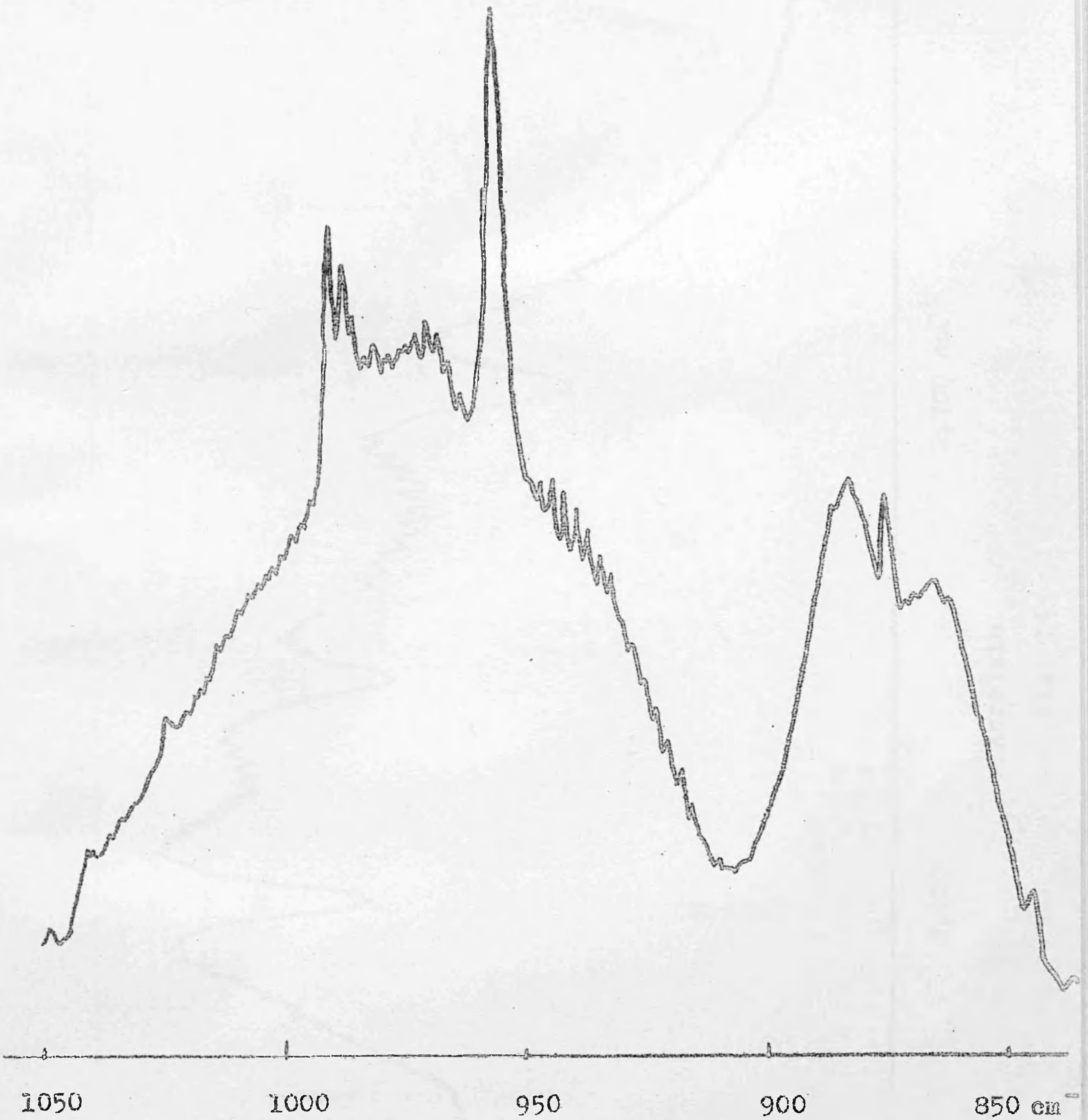
Acrolein, KBr Region

Fig. 11



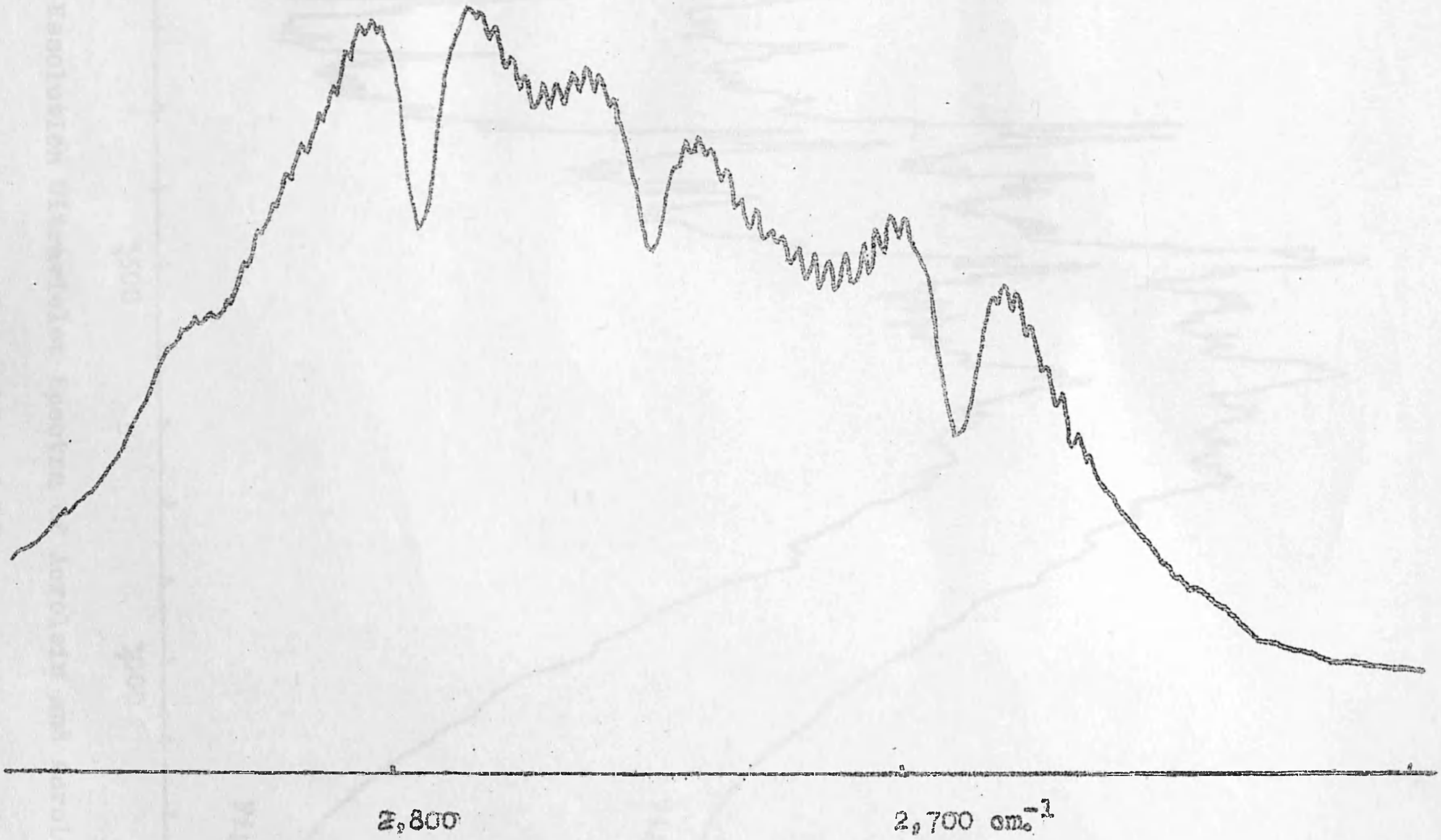
Acrolein

Fig. 12



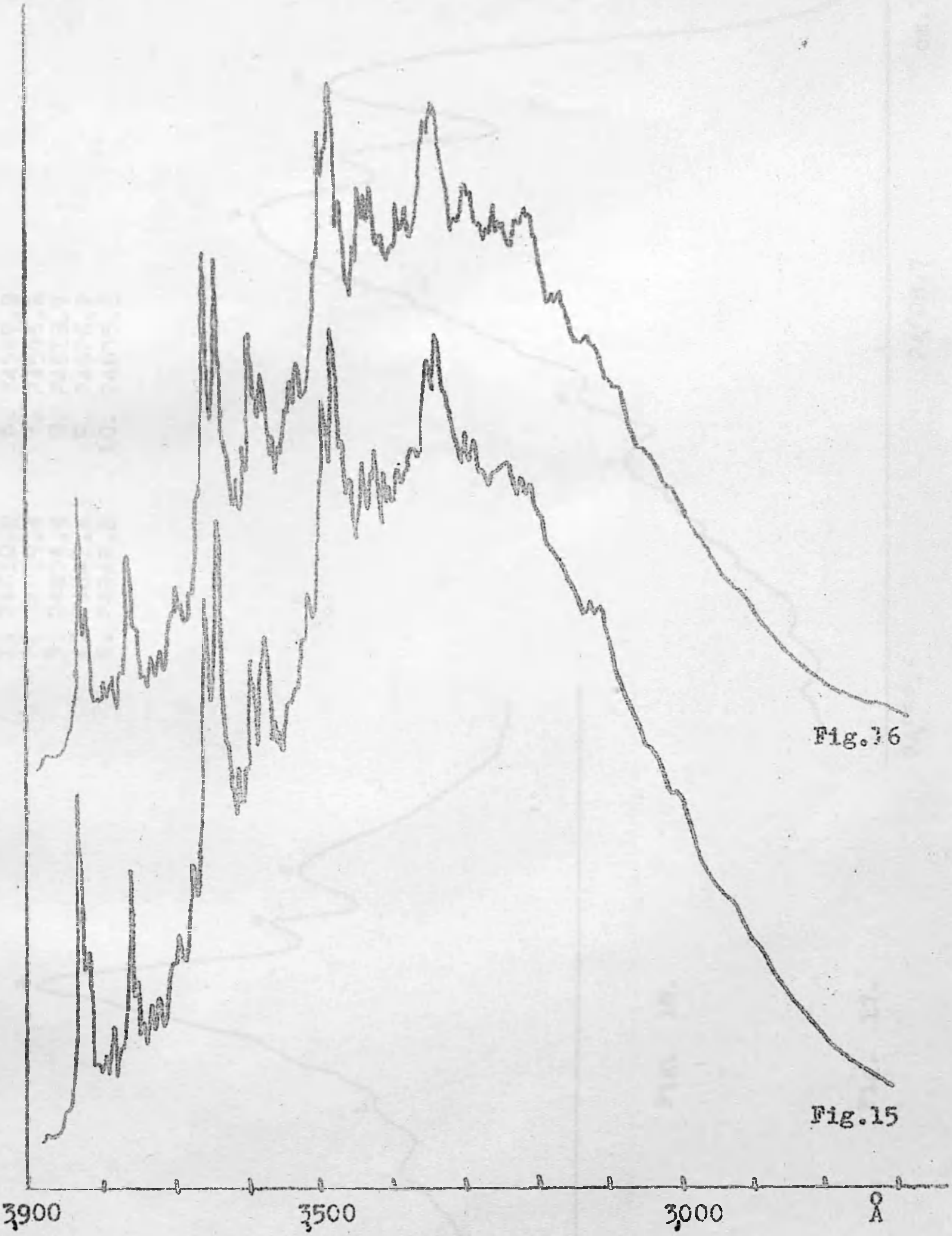
Acrolein - $d_1$

Fig. 13



Acrolein

Fig. 14



Low Resolution Ultraviolet Spectra of Acrolein and Acrolein - $d_1$

Figs. 15 and 16

1. 24810.9
2. 24819.4
3. 24834.4
4. 24842.4
5. 24848.8

6. 24587.8
7. 24596.6
8. 24618.7
9. 24626.2
10. 24635.6

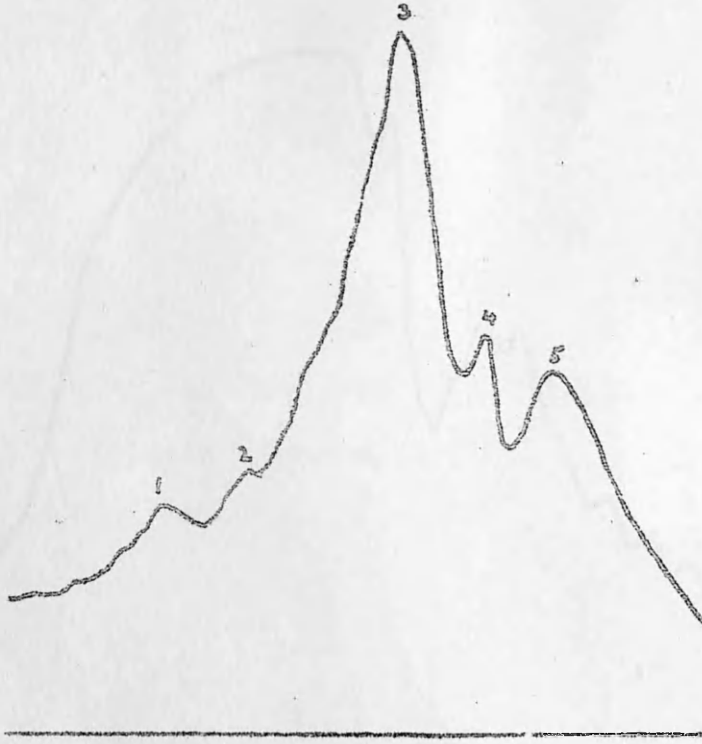


Fig. 18.

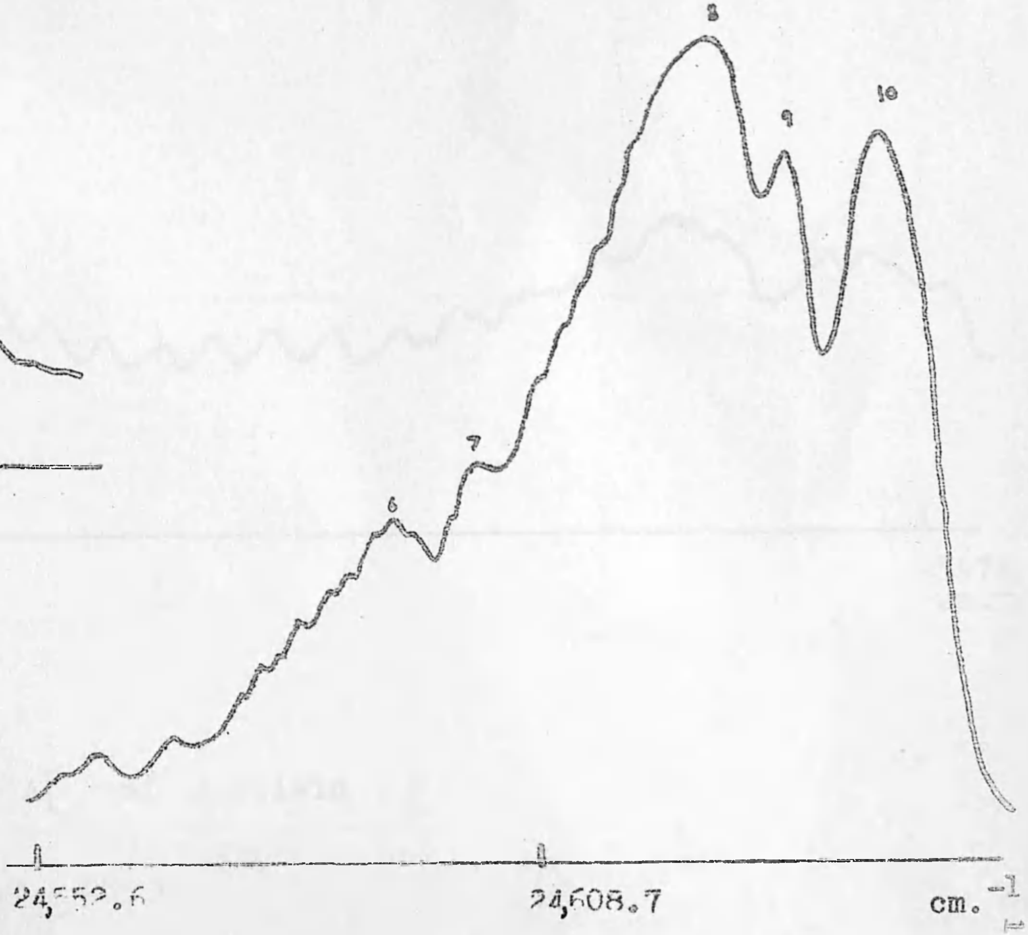
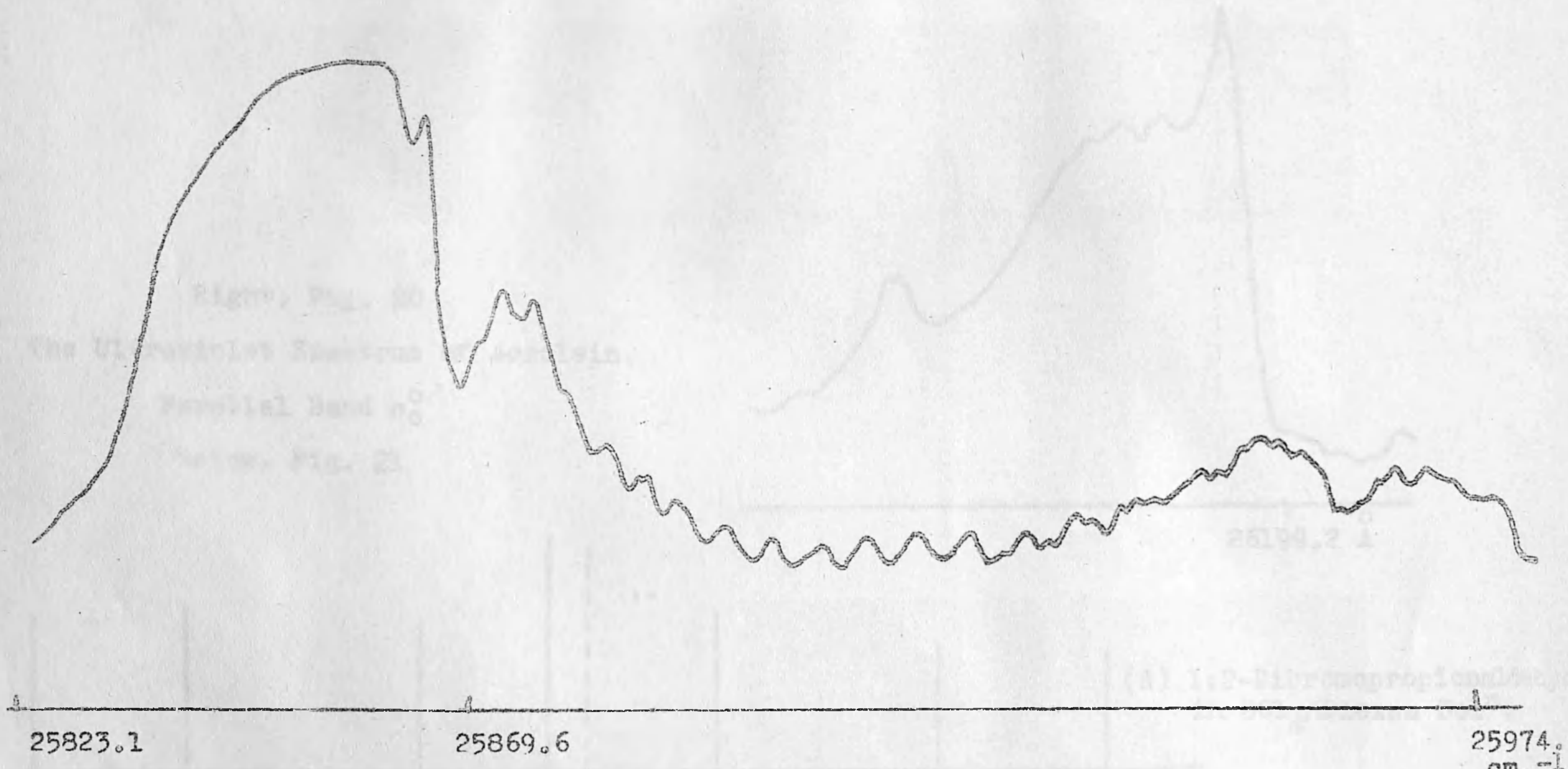


Fig. 17.



Bands $A_0^0$ and $A_1^0$ of Acrolein

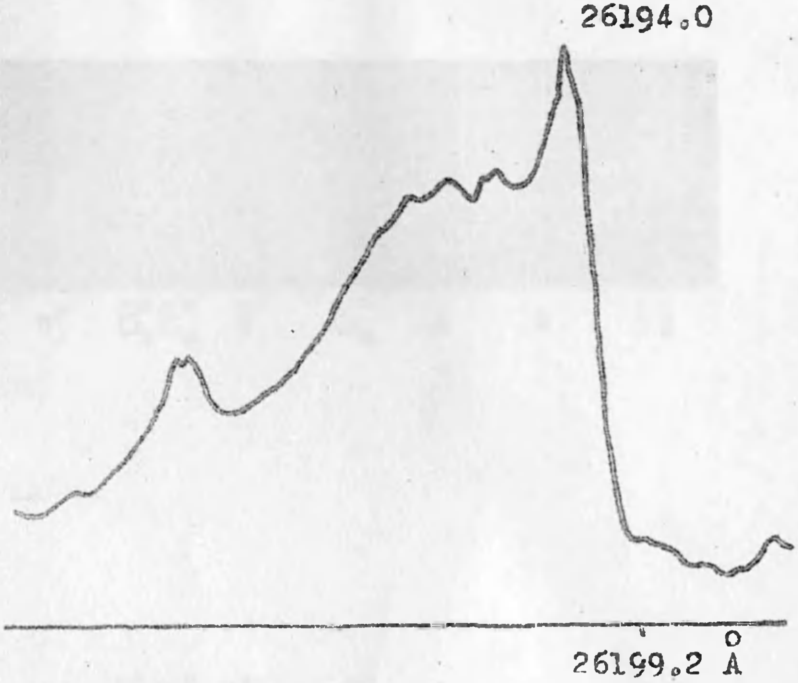
Fig. 19

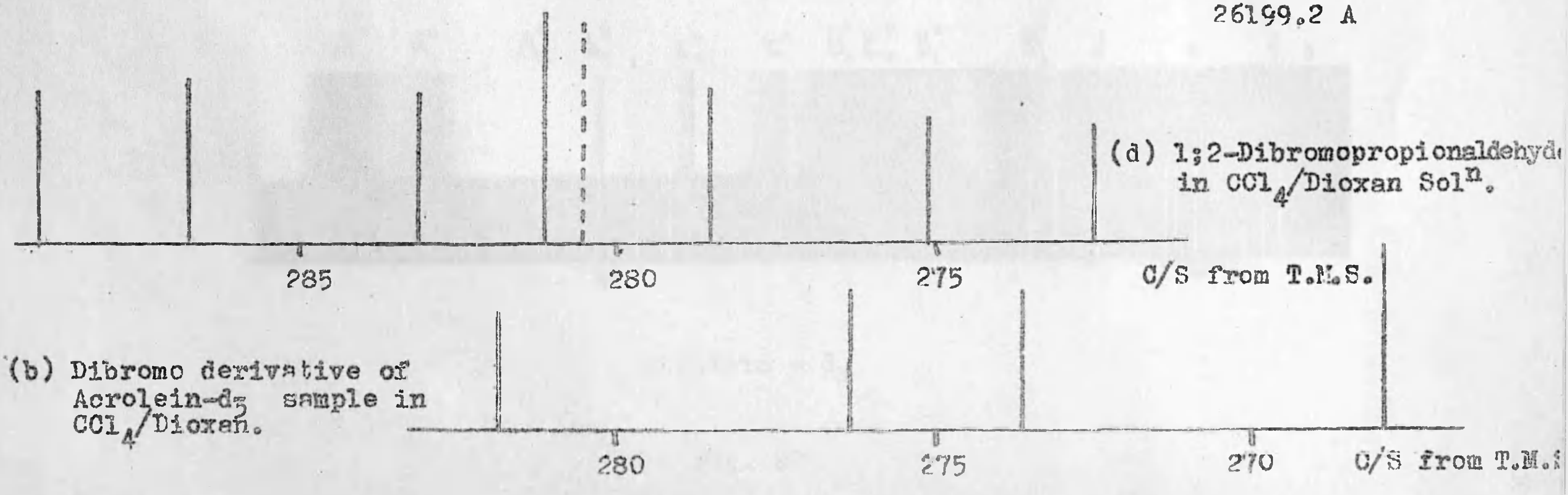
Right. Fig. 20

The Ultraviolet Spectrum of Acrolein,

Parallel Band $c_0^0$

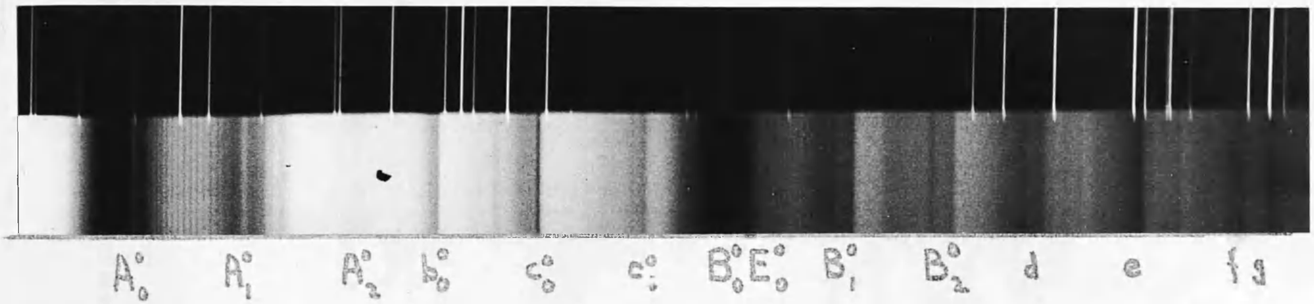
Below. Fig. 21



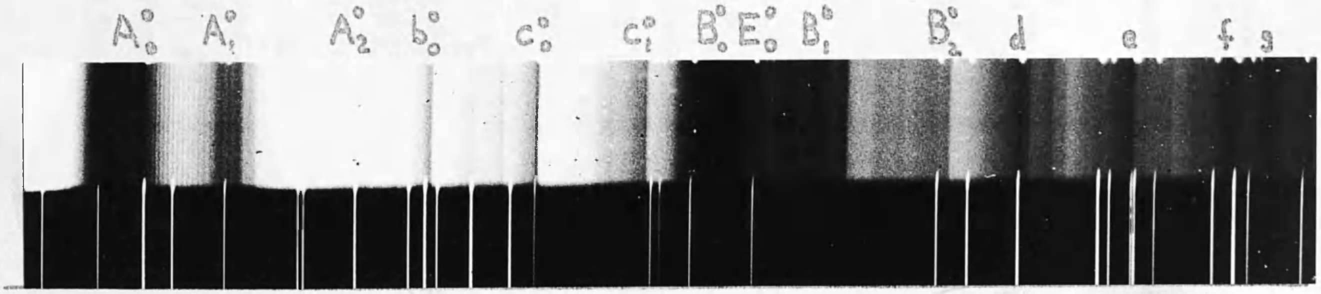


(d) 1;2-Dibromopropionaldehyd
in $CCl_4$/Dioxan Sol$^n$.

(b) Dibromo derivative of Acrolein-$d_3$ sample in $CCl_4$/Dioxan.



Acrolein



Acrolein - $d_1$

Fig. 22

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