ELECTRONIC TRANSITIONS DUE TO NONBONDING ELECTRONS IN CARBONYL, AZA-AROMATIC, AND OTHER COMPOUNDS

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Note added in proof: Dr. Sidman was killed in an automobile accident on June 21, 1958.

I. INTRODUCTION

Within the last ten years there has been a considerable increase in our understanding of the electronic spectra of polyatomic molecules. Theoretical and experimental investigations of the electronic structure and spectra of molecules have yielded much information about energies and symmetry properties of excited states, transition probabilities, vibrational and rotational energy levels in ground and in excited electronic states, and geometry and bonding in the various electronic states of complex molecules. In addition to the information about intramolecular properties, a large number of investigations have been concerned with the effects of molecular interactions of electronic spectra.

It is the purpose of this article to review some of the recent work on one particular type of electronic transition, namely, the type of transition which is commonly called $n \rightarrow \pi^*$. According to the simple LCAO-MO[2] description of an $n \rightarrow \pi^*$ transition, an electron is excited from a nonbonding orbital (n orbital), which to a great extent is localized on one atom in the molecule, into an antibonding orbital which is antisymmetric to reflection in the molecular plane (π^* orbital), and which extends over more than one atom in the molecule. This type of transition is usually low in intensity ($f \cong 10^{-4}$ to 10^{-2}), and is always the transition of lowest energy (longest wavelength) in carbonyl and in nitroso compounds. It is often the transition of lowest energy in aza-aromatic compounds and in some inorganic molecules and ions. Although the spectra of aromatic hydrocarbons can be well discussed by considering only the electrons in π orbitals, it is essential to consider electrons both in n orbitals and in π orbitals in order to understand the spectra of molecules containing oxygen and nitrogen atoms.

One of the very first efforts to classify the electronic spectra of complex molecules on the basis of empirical regularities is due to Burawoy (16). Burawoy classified the weak, long-wavelength absorption bands of compounds containing carbonyl, nitroso, azo, and other hetero groups as R-bands (*Radikalartige*), and thought that they were due to electronic transitions to an excited triplet state. In the light of subsequent work, it is now certain that the vast majority of the bands classified as R-bands by Burawoy do not involve the triplet state. In many cases, absorption bands due to singlet-triplet transitions have been observed at longer wavelengths and with lower intensities than the bands classified as R-bands by Burawoy. Although Burawoy's assignments and interpretations are not generally accepted by present workers, it is important to remember that he was one of the pioneers in the interpretation of the electronic spectra of complex molecules, and that many of the empirical regularities which have been developed by others were in fact first discovered by him.

The interpretation of electronic transitions in molecules as involving lone-pair or nonbonding electrons was first made by Mulliken (58) for carbonyl compounds and was extended to many carbonyl and thiocarbonyl compounds by McMurry (56, 57). Kasha (44) introduced the designation $n \rightarrow \pi^*$ for the transition involving the excitation of an electron from a nonbonding orbital

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[2] LCAO-MO = Linear Combination of Atomic Orbitals - Molecular Orbital.

to an antibonding pi orbital. Kasha's studies indicated the general occurrence of lowest $n \rightarrow \pi^*$ transitions in nitro-, nitroso-, azo-, and many aza- and related N-heterocyclic compounds. Halverson and Hirt (30), Rush and Sponer (86), and many others have extended Kasha's interpretation, and Platt (73, 74, 75, 76, 77) has summarized these results and has further elaborated on them. Kasha's work (44) has been instrumental in stimulating many workers in this field.

In order to distinguish between $n \rightarrow \pi^*$ transitions which are either allowed or forbidden by local symmetry, Platt (74, 75) has proposed a notation which will be employed throughout this paper. According to his notation, an $n \rightarrow \pi^*$ absorption transition which is allowed by *local* symmetry is given the label $^1W \leftarrow {}^1A$, whereas an $n \rightarrow \pi^*$ transition which is *unallowed* by local symmetry is given the label $^1U \leftarrow {}^1A$. The corresponding excited triplet states are ^3W and ^3U.

One advantage of this notation is its ability to distinguish between different types of $n \rightarrow \pi^*$ transitions irrespective of the group-theoretical notation which is based on the overall symmetry of the molecule. In the aliphatic carbonyl compounds, the constancy of the intensity of $n \rightarrow \pi^*$ transitions suggests that the *local* symmetry in the C=O group may be more important than the *overall molecular* symmetry in determining the intensity of the transition. The essential difference between $W \leftarrow A$ and $U \leftarrow A$ transitions is the following: if the transition density (49a) at the hetero atom contains a one-center term which transforms like a *local* electric dipole, i.e., a one-center term $(2s\,2p)$, then the transition is $W \leftarrow A$; if there is no one-center $(2s\,2p)$ term in the transition density, then the transition is $U \leftarrow A$. Thus, an $n \rightarrow \pi^*$ transition is $U \leftarrow A$ if the n orbital and the π^* orbital are both formed from $2p$ orbitals of different symmetry, whereas an $n \rightarrow \pi^*$ transition is $W \leftarrow A$ if the n orbital has some $2s$ character. An $n \rightarrow \sigma^*$ transition (see Section II,A) is $W \leftarrow A$ in the carbonyl compounds, since the σ^* orbital has some $2s$ character at the oxygen atom. The empirical criteria by which the transitions can be distinguished will be discussed in the following sections. It is heartily recommended here that future workers employ the Platt symbols wherever possible. The reader should note that a $^1U \leftarrow {}^1A$ transition may be either allowed or forbidden by molecular symmetry, and that the same is true for a $^1W \leftarrow {}^1A$ transition. The Platt notation and the group-theoretical notation are therefore complementary.

II. Review of Recent Work (to September, 1957)

A. General Theory

The first attempt to interpret the spectra of carbonyl compounds by molecular orbital theory was made in 1935 by Mulliken (58). Mulliken suggested that the lowest ionization potential of formaldehyde is due to the removal of an electron in a nonbonding $2p$ orbital localized on the oxygen atom, and further suggested that the (lowest) 2900 A. absorption band system of formaldehyde involves the nonbonding orbital. The analogy between the spectra of the $\diagdown$C=O and the $\diagup$ $\diagdown$C=S groups was discussed. After considering the various possibilities, Mulliken $\diagup$

was unable to decide whether the 2900 A. band system of formaldehyde was due to a transition which is allowed by molecular symmetry, with a transition moment in the plane of the molecule and perpendicular to the C=O axis, or to a transition which is forbidden by molecular symmetry. The transition which is allowed by molecular symmetry in formaldehyde also is allowed by local symmetry and is therefore $^1W \leftarrow {}^1A$. It involves the excitation of an electron from the $2p$ orbital localized on the oxygen atom (n orbital) to an antibonding orbital which contains some $2s$ character at the oxygen atom, which is localized in the C=O bond, and which is symmetric to reflection in the molecular plane (σ^* orbital). The transition which is forbidden by molecular symmetry in formaldehyde is also forbidden by local symmetry and is therefore $^1U \leftarrow {}^1A$. It involves excitation of an electron from the n orbital to an antibonding orbital which contains *no* $2s$ character, which is localized in the C=O bond, and which is antisymmetric to reflection in the molecular plane (π^* orbital). A schematic diagram of the molecular orbitals of formaldehyde is given in figure 1.

In order to help decide which of the two possible assignments was the correct one, McMurry (56) calculated the intensity which is predicted for the symmetry-allowed $^1W \leftarrow {}^1A$ transition by several approximate treatments. Assuming that the bands near 2900 A. are due to the $^1W \leftarrow {}^1A$ transition, the calculated oscillator strength (f) ranged from 0.013 to 0.031, depending on the assumptions about the form of the wave functions. The value which is observed for the corresponding transition of acetone at 2900 A. is $f = 4 \times 10^{-4}$. The experimental oscillator strength is too low to be consistent with the $^1W \leftarrow {}^1A$ assignment. McMurry therefore assigned the 2900 A. bands to the forbidden $^1U \leftarrow {}^1A$ transition and suggested that the 1900 A. transition of acetone is $^1W \leftarrow {}^1A$. The observed oscillator strength is about 0.02 for the 1900 A. transition of acetone. The
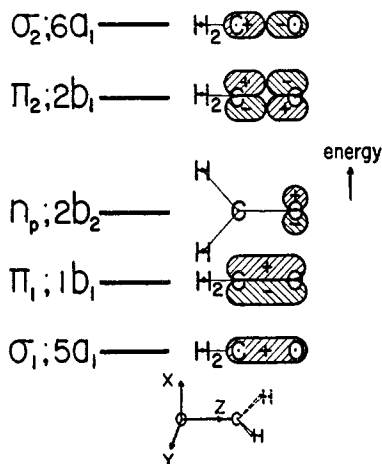

FIG. 1. Schematic molecular orbitals for formaldehyde. The carbon–hydrogen bonding orbitals and inner shell orbitals lie below σ_1 and the carbon–hydrogen antibonding orbitals lie above σ_2. The molecular orbitals are labelled by the notation used in this paper ($\sigma_1, \cdots , \sigma_2$) as well as by the notation ($5a_1, \cdots , 6a_1$) recommended by Mulliken (59).

$\pi \rightarrow \pi^*$ transition should be much more intense than $f = 0.02$. McMurry assigned the intense 1550 A. transition of various ketones to the $\pi \rightarrow \pi^*$ transition.

McMurry (57) was able to identify the weak $^1U \leftarrow {}^1A$ transition as the longest wavelength transition in several conjugated aldehydes, ketones, and quinones. The $^1U \leftarrow {}^1A$ transition moves to longer wavelengths with increasing conjugation. In molecules in which the $^1U \leftarrow {}^1A$ transition is no longer rigorously forbidden by symmetry, the intensity is nevertheless low. McMurry suggested that the main part of the intensity should still be derived from vibrational-electronic interaction.

However, another interpretation of the low intensity of $^1U \leftarrow {}^1A$ transitions was given by Platt (73). Platt pointed out that the difference in the spatial properties of the n and the π^* orbitals should lead to a low intensity for $^1U \leftarrow {}^1A$ transitions even when the molecular symmetry is such that no transitions are forbidden by symmetry. Such a weak transition is, in a sense, overlap-forbidden, even though it may be symmetry-allowed. In quantum-mechanical language, the n and the π^* orbitals do not simultaneously both possess large amplitudes, of either positive or negative sign, at any regions of space, since their lobes point in different directions. The integrand in the one-electron transition-moment integral,

$$\int n(1)R(1)\ \pi^*(1)\ dv(1)$$

is everywhere small if n and π^* are $2p$ orbitals which point in different directions' and the intensity of the $^1U \leftarrow {}^1A$ electronic transition is therefore low. Thus, it is possible to explain how a $^1U \leftarrow {}^1A$ electronic transition can show all the vibrational characteristics of a transition which is allowed by symmetry and in which there is no contribution of vibrational-electronic interaction to the total intensity, and yet be quite weak.

It has been observed by Burawoy (16), by Baba (3), and by Nagakura (60) that substituents which are able by resonance to donate electrons to the π-conjugated system generally shift the $^1U \leftarrow {}^1A$ transition to higher energies (shorter wavelengths). Nagakura (60) has interpreted this intramolecular blue shift in terms of the simple LCAO-MO picture of the $^1U \leftarrow {}^1A$ transition. In the $^1U \leftarrow {}^1A$ transition of the $\diagdown$C=O group, electronic charge is transferred from oxygen to carbon. Electron-donating groups attached to the carbon atom, such as —Cl, —OCH$_3$, and —N(CH$_3$)$_2$, raise the energy of the excited state relative to the energy of the ground state and produce an intramolecular blue shift of the $^1U \leftarrow {}^1A$ transition. Orgel (67) has further discussed the importance of electronic redistribution in $^1U \leftarrow {}^1A$ transitions.

B. SEMIEMPIRICAL CALCULATIONS OF THE ENERGY OF $U \leftarrow A$ TRANSITIONS

Although the early papers by Mulliken and by McMurry have given very satisfactory qualitative discussions of $U \leftarrow A$ transitions, further attempts to

treat these transitions semiquantitatively have only recently been made. Semi-empirical calculations have been remarkably successful in treating the $\pi \to \pi^*$ transitions of the aromatic hydrocarbons (68, 69, 70, 78, 79). Very recently, the semiempirical methods have been employed by several workers to calculate the energy of the $n \to \pi^*$ ($U \leftarrow A$) and the $\pi \to \pi^*$ transitions of conjugated carbonyl compounds. Anno and Sadô (2) have applied the Pariser–Parr treatment to formaldehyde. The results which they have obtained by using the semiempirical ASMO-CI[3] procedure are in good agreement with experiment. In a similar calculation, except for the neglect of configurational interaction, Anno, Matubara, and Sadô (1) have discussed the $n \to \pi^*$ ($U \leftarrow A$) and the $\pi \to \pi^*$ transitions of p-benzoquinone, again obtaining reasonably good agreement with experiment.

A simplified semiempirical SCF-MO[4] treatment of formaldehyde, glyoxal, and p-benzoquinone has been given by Sidman (95), who has attempted to calculate the π-ionization potentials and the energy of the $n \to \pi^*$ ($U \leftarrow A$) and the $\pi \to \pi^*$ transitions. The calculated values of the energies of the low excited states are in reasonably good agreement with experiment. In Sidman's SCF-MO calculations, it was necessary to include a certain amount of configurational interaction in order to obtain good values for the energies of the excited U states. Sidman has shown how the difference in spatial properties of the n and the π^* orbitals is related both to the low energy of the ^1U state and to the small (about 0.4 e.v.) singlet-triplet separation between ^3U and ^1U. Reid (82a) has also discussed this problem.

Parks and Parr (71) have given a semiempirical treatment of formaldehyde in which the six electrons in the σ_{C-O} bonding, π_{C-O} bonding, and n_O nonbonding orbitals are treated explicitly.

In two brief letters, Goodman and Shull (27) have discussed possible modifications of the naive molecular orbital method to include a semiempirical treatment of $n \to \pi^*$ transitions. Further developments of these ideas are awaited with interest.

C. SOLVENT EFFECTS ON $U \leftarrow A$ AND $W \leftarrow A$ TRANSITIONS

It was observed by Scheibe (89, 90) and others that the long-wavelength, low-intensity absorption band of acetone and other carbonyl compounds shifts to shorter wavelengths in solvents of high dielectric constant. Kasha (44) suggested that this "blue shift" in solvents of high dielectric constant could be used to characterize $n \to \pi^*$ transitions. McConnell (54) further applied this empirical criterion to the spectra of various molecules, and gave an explanation of the blue-shift phenomenon. According to him, the solvent orientation in a polar solvent is favorable to the electronic distribution in the ground state of the solute molecule. The $n \to \pi^*$ transition in the solute molecule leads to a considerable change in the charge distribution. The solvent molecules cannot reorient during the time required for the transition to occur, according to the Franck–Condon principle. The energy of the ground state is thus lowered by

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[3] ASMO-CI = Anti-Symmetrized Molecular Orbitals - Configurational Interaction.

[4] SCF-MO = Self-Consistent Field - Molecular Orbital.

solvation more than the energy of the excited state, and the $n \rightarrow \pi^*$ transition shifts to shorter wavelengths as the polarity of the solvent increases.

Brealey and Kasha (14) have convincingly demonstrated that in hydroxylic solvents the blue shift of $^1U \leftarrow {}^1A$ transitions is due primarily to hydrogen bonding of the nonbonding electrons by the hydroxylic solvent, and that in these cases specific hydrogen bonding is more important than any general effect which depends on dielectric constant. Their careful spectral measurements have shown that essentially two molecular species are involved in the absorption spectra of benzophenone and pyridazine in ethanolic solution. These two species are the ordinary solvated molecule, whose absorption spectrum in ethanol is very similar to the spectrum in an inert hydrocarbon solvent, and the hydrogen-bonded molecule, whose spectrum is shifted some 100 to 1200 cm.$^{-1}$ to shorter wavelengths, with accompanying blurring out of the vibrational structure. Brealey and Kasha have found that the shift in the $^1U \leftarrow {}^1A$ band is approximately equal to the energy of the hydrogen bond in the ground state. Hydrogen bonding in the excited state is therefore expected to be very weak or nonexistent in these cases.

Pimentel (72) has suggested that residual hydrogen bonding in the excited state may still be considerable. He has pointed out the importance of the Franck–Condon principle in discussing the blue shift produced by intermolecular hydrogen bonding. The quantitative agreement between the blue shift and the energy of the hydrogen bond which Brealey and Kasha obtained may therefore be fortuitous, although the qualitative features of their discussion are not invalidated. Pimentel stresses the desirability of determining if possible the shift of the 0–0 band rather than the shift of the absorption band maximum.

Bayliss and McRae (4) have attempted to enumerate the various effects which contribute to the shift of absorption spectra in solution. It is likely that specific hydrogen bonding is the most important effect in hydroxylic solvents, although in other cases the various other interactions may be quite important.

Mataga and Tsuno (52) have found that hydrogen bonding increases the fluorescence yield of some aza-aromatic compounds in solution. They suggest that some sort of interaction between the n electrons and the π electrons may lead to internal quenching of the fluorescence, and that this is impeded by hydrogen bonding to the n electrons. A more specific explanation is that the upper state of the $n \rightarrow \pi^*$ transition (^1U or ^1W) is shifted to higher energies by hydrogen bonding, whereas the upper state of the $\pi \rightarrow \pi^*$ transition (^1L_b(?)) is relatively unaffected by hydrogen bonding. The ^1U and ^1W upper states in the aza-aromatic compounds generally do not show fluorescence, whereas the ^1L_b states of many aromatic hydrocarbons do fluoresce (4a, 77). (Note, however, that the ^1U and ^3U states of many carbonyl compounds *do* show fluorescence and/or phosphorescence, respectively.) If the ^1U or ^1W upper state lies below the ^1L_b state, the aza-aromatic compound will usually be nonfluorescent. Hydrogen bonding may shift the ^1U or ^1W state so that it lies above the ^1L_b state, in which case the compound may then fluoresce (49, 77).

D. THE ANALYSIS OF THE ABSORPTION AND FLUORESCENCE BANDS OF THE ^1U—^1A,
$^1A_2$—$^1A_1$ TRANSITION IN FORMALDEHYDE

1. Recent developments

The first measurements of the 2900 A. absorption bands of gaseous formaldehyde were made by Henri and Schou (33). The fluorescence bands were recorded and partially analyzed by Herzberg and Franz (35) and by Gradstein (28). Dieke and Kistiakowsky (21) gave a rotational analysis of some of the stronger absorption bands in the 2900 A. transition. They showed that the oscillating transition moment for some of the prominent bands is in the plane of the molecule and is perpendicular to the twofold axis of symmetry. However, it was not possible at that time to give a convincing interpretation of the relation between the bands in the fluorescence and in the absorption spectra. The problem has recently been solved, owing in large measure to the analyses by Brand, who has employed only relatively modest spectrographic apparatus in his work. Brand (10) found evidence in the fluorescence spectrum for Coriolis interaction between the out-of-plane CH_2 wagging vibration, ν_6, and the in-plane CH_2 asymmetric rocking vibration, ν_5. In a vibrational analysis of the fluorescence spectra of H_2CO and D_2CO, Brand (7) showed evidence for long progressions of the ν_6 vibration. This was further interpreted by Walsh (103) as evidence for the nonplanarity of the H_2CO molecule in its excited state. Walsh showed that a very simple molecular orbital description predicts that the $U \leftarrow A$ transition of formaldehyde should lead to such a change in molecular geometry in the excited state. In a comprehensive paper (8), Brand has given a detailed vibrational analysis of the absorption and fluorescence spectra of H_2CO, D_2CO, and HDCO. He has also given a partial rotational analysis of the bands and an interpretation of many of their spectral features. High-resolution studies of the fluorescence bands of formaldehyde have been carried out by Robinson (83). Further high-resolution studies of the absorption spectrum of gaseous formaldehyde are currently under investigation (85).

2. Results of the recent spectroscopic investigations of formaldehyde

Although it is likely that further measurements will lead to revision and refinement of some of the conclusions, the main features of the absorption and fluorescence bands of formaldehyde are at present reasonably well understood (8, 83). The molecule is planar in its ground state, but is pyramidal in the equilibrium nuclear configuration of the upper state, which belongs to the representation $^1A_2$ of C_{2v} and $^1A''$ of C_s. The angle between the plane of the CH_2 nuclei and the C—O axis is approximately 20°. The carbon–oxygen bond length increases from 1.22 A. in the ground state to 1.32 A. in the equilibrium nuclear configuration of the upper state. The barrier to inversion doubling in the upper state is roughly 650 cm.$^{-1}$ The 0–0 transition from the vibrationless lower state to the lowest vibrational level of the upper state is forbidden by symmetry selection rules, even for the bent upper state. It nevertheless does appear weakly in absorption as a parallel band, with oscillating transition moment parallel to

the carbon–oxygen axis, which is the axis of least inertia. The 0–0 band is called a_0 by Brand (8). Its frequency is 28196 cm.$^{-1}$ in H_2CO and 28309 cm.$^{-1}$ in D_2CO. The 0^+ and 1^+ levels of the ν_6 inversion doublet are the origins of progressions of the symmetric C—O stretching vibration, ν_2, and the symmetric CH_2 deformation vibration, ν_3, in the absorption spectrum. These bands are weak parallel bands. The strong perpendicular bands in absorption are due to progressions of the symmetric CH stretching vibration, ν_1, and the ν_2 and the ν_3 vibrations, on the 0^- and 1^- levels of the ν_6 inversion doublet (figure 2). Long progressions in ν_2 are very prominent in absorption.

The fluorescence spectrum shows progressions in ν_2 and in ν_6. All fluorescence bands are perpendicular bands. The levels of the ν_6 vibration are perturbed by Coriolis coupling with ν_5. The 0^+ and $(0^+ + \nu_2)$ levels of the upper state are the strong origins of the fluorescence spectrum. Much weaker transitions originate from the 0^- and from the $(0^+ + 2\nu_2)$ levels. The 1^+ and 1^- levels of the upper state give rise only to very weak fluorescence bands. This has been attributed to predissociation in this region of the potential energy surface (12).

The absorption spectrum of formaldehyde contains at its long-wavelength end several weak bands which do not decrease in intensity as the temperature is lowered. These bands have been assigned to the $^3U \leftarrow {}^1A$, $^3A_2 \leftarrow {}^1A_1$ transition (8, 18, 83). The upper state of this band system also shows inversion doubling, which indicates that the excited triplet state, like the excited singlet state, is pyramidal. The 0^+ level of the ν_6 inversion doublet has been assigned at 25200 cm.$^{-1}$ in H_2CO and at 25321 cm.$^{-1}$ in D_2CO. The triplet-singlet transition appears only in absorption, and not in emission.

Walsh (103), Brand (8), and Robinson (83) have discussed the electronic structure of the formaldehyde molecule in its excited state. The carbon–oxygen bond length in the excited state (1.32 A.) corresponds to a three-electron bond and is similar to the bond length in the ground state of formic acid. The molecule
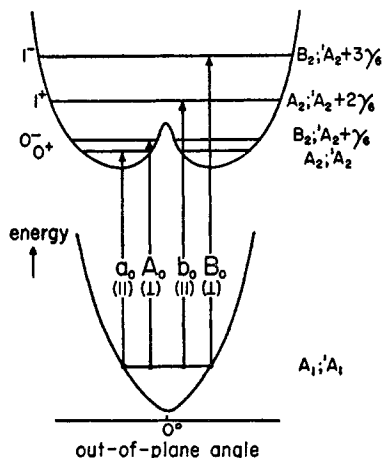

FIG. 2. Schematic diagram of some of the vibrational transitions in the $^1A_2 \leftarrow {}^1A_1$, $n_p \rightarrow \pi_2$ electronic transition of formaldehyde. After Brand (8).

becomes pyramidal in its excited state in order to obtain some relief from anti-bonding. The orbital energy of the $\pi_{CO}*$ orbital (π_2; $2b_1$) falls rapidly as the molecule becomes pyramidal. This orbital is antibonding in the planar form, but becomes increasingly nonbonding in the pyramidal form.

3. The intensity of the $^1U \leftarrow {}^1A$ transition in formaldehyde

Pople and Sidman (80) have discussed the interaction between electronic and nuclear motions in the $^1U \leftarrow {}^1A$ transition of formaldehyde. Using a simplified semiempirical molecular orbital model, they have predicted that the most important contribution to the intensity of the forbidden $^1U \leftarrow {}^1A$, $^1A_2 \leftarrow {}^1A_1$ transition should arise from vibrational-electronic interaction involving the ν_6 out-of-plane vibration. This would give rise to perpendicular bands with transition moment in the molecular plane, in agreement with observations. The total f-number (oscillator strength) due to bands of this polarization is calculated to be of the order of 10^{-4}. According to Pople and Sidman's calculations, it is possible that the weak parallel bands, including the 0–0 band, a_0, may be due to rotational-electronic interaction involving rotation around the symmetry axis. If so, an abnormal intensity dependence of the K structure in the parallel bands is to be expected. Experimental observations on this point are being made by Robinson (85). Another possible explanation is that the weak parallel bands are due to a magnetic dipole transition. The analysis of the rotational structure of a_0 should show which of these explanations is the correct one.

E. $U \leftarrow A$ TRANSITIONS IN OTHER CARBONYL COMPOUNDS

The absorption spectra of carbonyl compounds in solution have been discussed by McMurry (57), who has given references to data previous to 1941. Since that time, the $U \leftarrow A$ transitions of several carbonyl compounds have been examined under conditions which give higher spectral resolution. Vibrational structure, and in some cases rotational structure, has been resolved and analyzed. The studies of the absorption and fluorescence spectra of crystals at very low temperatures have contributed a body of precise data from which vibrational analyses can sometimes be deduced. In addition, the study of the spectra of gaseous molecules has been useful. Several carbonyl compounds of particular interest will be discussed briefly in this section, with emphasis on some of the details of the electronic transitions.

1. Acetaldehyde

Rao and Rao (81) have attempted to analyze the very complex band system of acetaldehyde near 3000 A. They have studied the absorption bands of gaseous acetaldehyde and have given a vibrational analysis of the bands. These bands are much more complex than the corresponding bands of formaldehyde, owing very probably to the CH_3 torsional vibration. The bands merge to a continuum at the short-wavelength end. Rao and Rao assign the band at 3201.4 A as the 0–0 transition, and they assign several vibrational frequencies in the upper state.

The complexity of the bands for acetaldehyde precludes a complete and convincing analysis such as has been given for formaldehyde. In particular, it is not possible thus far to say if the molecule changes its geometry in the upper electronic state, if vibrational-electronic interaction contributes to the intensity of this transition, or if the singlet-triplet bands appear in absorption.

2. Acetone

The bands due to the $^1U \leftarrow {}^1A$ transition in acetone are much more complex than in acetaldehyde. The absorption (63) and fluorescence (50) spectra of acetone still await analysis.

3. Acrolein and crotonaldehyde

The absorption spectrum due to the $^1U \leftarrow {}^1A$ transition in acrolein between 4100 A. and 3200 A. is very sharp and shows resolved rotational structure (22). The C=O stretching frequency is prominent in absorption, and is approximately 1260 cm.$^{-1}$ in the upper state. The corresponding transition in crotonaldehyde, $CH_3CH=CH-CH=O$, is more diffuse than in acrolein, $H_2C=CH-CH=O$.

4. Glyoxal

Brand (10) has given convincing vibrational and rotational analyses of the absorption and fluorescence bands of $(HCO)_2$ and $(DCO)_2$. The 0–0 band of the $^1U \leftarrow {}^1A$ transition of glyoxal appears at 21977 cm.$^{-1}$ The 0–0 band is allowed by molecular symmetry, but the local symmetry is the same as in formaldehyde, and the transition is still $^1U \leftarrow {}^1A$. The rotational analysis shows that the transition moment of the 0–0 band is perpendicular to the molecular plane, in agreement with theoretical predictions for a $^1U \leftarrow {}^1A$ transition which is allowed by molecular symmetry. Vibrational-electronic interaction involving the out-of-plane C—H wagging vibration contributes to the intensity of some of the bands in this transition and gives rise to bands with transition moment in the molecular plane. Brand has assigned several vibrational frequencies in the upper state. The C=O symmetric stretching frequency in glyoxal is 1391 cm.$^{-1}$ in the ^1A_u excited state (^1U) and 1742 cm.$^{-1}$ in the ^1A_g ground state (^1A). The singlet-triplet transition appears weakly both in absorption and in emission. The 0–0 band of the $^3U \leftarrow {}^1A$ transition is at 19544 cm.$^{-1}$ in $(DCO)_2$.

5. Biacetyl

The absorption and emission spectra of gaseous biacetyl are complex and diffuse, and are not capable of detailed analyses. However, the spectra of crystalline $(CH_3CO)_2$ and $(CD_3CO)_2$ at 20°K. are quite sharp, and vibrational analyses of these bands have been given by Sidman and McClure (97). A $^3U \leftarrow {}^1A$ absorption transition has been identified and vibrationally analyzed. The 0–0 band is at 20421 cm.$^{-1}$ in biacetyl at 4°K. The intense green phosphorescence (47a), due to a $^3U \rightarrow {}^1A$ transition, has also been analyzed (97). The $^1U \leftarrow {}^1A$ transition (0–0 band at 22873 cm.$^{-1}$) is strong in absorption relative to the $^3U \leftarrow {}^1A$ transition, but fluorescence from the excited singlet state ($^1U \rightarrow {}^1A$) is very

weak, whereas phosphorescence from the excited triplet state ($^3U \rightarrow {}^1A$) is quite intense. This is to be contrasted with glyoxal.

Another $^1U \leftarrow {}^1A$ transition appears at shorter wavelengths, with 0–0 band at 31475 cm.$^{-1}$ This transition probably involves excitation of an electron into a more highly antibonding π orbital than the transitions at longer wavelengths. There is evidence, both spectral and photochemical (64), that the upper state of the 31475 cm.$^{-1}$ system predissociates. The spectral and photochemical data for this molecule lead to similar conclusions about the nature of the various ^1U excited states. Sidman and McClure (97) have given assignments for many vibration frequencies of $(CH_3CO)_2$ and $(CD_3CO)_2$ in the ground state and low excited states.

The $^3U \leftarrow {}^1A$ absorption transition has been observed in solution by Forster (25).

6. Oxalyl chloride

The absorption spectrum of oxalyl chloride has been analyzed by Sidman (91). The 0–0 band of a $^1U \leftarrow {}^1A$ transition is very probably the band at 27178 cm.$^{-1}$, which is the origin of progressions of an upper-state vibrational frequency of 1420–1460 cm.$^{-1}$ This vibrational frequency is assigned to the symmetric C=O stretching vibration in the upper state. The temperature dependence of the absorption spectrum shows evidence for a rapid reversible equilibrium involving oxalyl chloride. The equilibrium is shifted at higher temperature in the direction which decreases the concentration of the oxalyl chloride molecules which give the sharp spectrum discussed above. At the same time, the concentration of some molecule which has a continuous absorption spectrum in the same region increases. Dependence of the Raman and infrared spectra of oxalyl chloride on temperature has also been observed (43, 88). These results have been interpreted as evidence for rotational isomerism around the C—C bond in oxalyl chloride.

The $^1U \leftarrow {}^1A$ transition in oxalyl chloride is shifted more than 4000 cm.$^{-1}$ to higher frequencies compared with the corresponding transition in glyoxal or in biacetyl. This has been attributed to the internal blue shift produced by the electron-donating chlorine atoms (60, 91). Another possible explanation is that there is less conjugation in oxalyl chloride than in glyoxal. The comparison between the bonding in glyoxal and in oxalyl chloride has been discussed (91).

7. p-Benzoquinone

Sidman (92) has studied the spectra of single crystals of p-benzoquinone at 20°K. Two $^1U \leftarrow {}^1A$ transitions and one $^3U \leftarrow {}^1A$ transition have been identified in absorption between 4000 A. and 5000 A. As McMurry has commented (57), the presence of two carbonyl groups should give rise to two $^1U \leftarrow {}^1A$ transitions. No fluorescence or phosphorescence was observed when the crystals were excited with blue or with ultraviolet light at 20°K., even though the absorption spectra are very sharp. It is possible that radiationless transitions from the ^1U and ^3U states to the ground state are very rapid in p-benzoquinone. An attempt has been made to analyze the irregular vibrational and lattice structure which appears in the absorption spectrum.

It should be noted (96) that the labelling of the p- and b-axes in Sidman's work is incorrect and should be reversed. The disagreement between Sidman's results and those of Brand and Goodwin (11) is thereby ended, and the apparent discrepancy between theoretical calculations and experimental results is thus explained.

Nagakura and Kuboyama (61) have studied the blue-shift effect of the solvent on p-benzoquinone in solution.

8. 9,10-Anthraquinone and 1,4-naphthoquinone

Sidman (93) has studied the $^1U \leftarrow {}^1A$ transitions of these crystals at 4°K. The $^1U \leftarrow {}^1A$ transitions give very sharp spectra in the molecular crystals, but the spectra are extremely complex and appear to be devoid of any regular progressions of vibrational frequencies. There is some evidence for the presence of two electronic transitions, probably both singlet-singlet, in the 4200 A. region of the spectrum. The $^1U \leftarrow {}^1A$ transition(s) shifts to higher frequencies in the sequence p-benzoquinone, 1,4-naphthoquinone, 9,10-anthraquinone. This would be difficult to understand if the length of effective conjugation really increased as more benzene rings become part of the conjugated system. It is therefore likely that the $^1U \leftarrow {}^1A$ transition is localized in the one quinonoid ring and that the shift to higher frequencies is caused by the electron-donating benzene rings which are fused to the quinonoid ring. The attempt to interpret the spectra on the basis of the FEMO[5] model which is given in Sidman's paper is probably incorrect.

Phosphorescence spectra have also been reported (47a).

9. Benzaldehyde and benzophenone

Imanishi, Semba, Ito, and Anno (39) have measured and analyzed the long-wavelength absorption spectrum of benzaldehyde. Robinson (84) has observed the corresponding emission transition in a high-frequency electrical discharge. From the combined results, it is clear that the 0-0 band of the transition is at 26914 cm.$^{-1}$ and that the $C{=\!=}O$ stretching vibration frequency is 1732 cm.$^{-1}$ in the ground state and 1310 cm.$^{-1}$ in the excited state. The transition is almost certainly $^1U-{}^1A$, although some weak bands may possibly be due to the $^3U-{}^1A$ transition.

McClure and Hanst (53) have studied the absorption and emission spectra of single crystals of benzophenone, $(C_6H_5)_2CO$, at 20°K. They report that the $^1U \leftarrow {}^1A$ transition oscillator appears to lie in the plane of the rings, and not perpendicular to the plane of the rings. It is possible that this anomaly may be due to vibrational-electronic interaction, or to crystal-induced mixing of different electronic states, or to both. The 0-0 band of the $^1U \leftarrow {}^1A$ transition is at 26580 cm.$^{-1}$ and the $C{=\!=}O$ stretching frequency is 1240 cm.$^{-1}$ in the upper state. The emission which is excited by ultraviolet radiation is probably due to the $^3U \rightarrow {}^1A$ transition with 0-0 band at 23800 cm.$^{-1}$ The $C{=\!=}O$ stretching frequency in the ground state is 1740 cm.$^{-1}$

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[5] FEMO = Free Electron Molecular Orbital.

10. Carboxyl and amide groups

The intramolecular blue shift of $n \rightarrow \pi^*$ transitions produced by electron-donating substituents is very important in the spectra of the carboxyl (—COOH) and amide (—CONH$_2$) groups. The $^1U \leftarrow {}^1A$ transition of the C=O group in formaldehyde is at 2900 A. (λ_{max}), whereas the corresponding transition in the carboxyl group (87) and in the amide group (34, 48) is near 2100 A. In peptides, the $^1U \leftarrow {}^1A$ transition is completely hidden by the stronger $\pi \rightarrow \pi^*$ transition near 1900 A. (31). In the formate ion (HCOO$^-$) the $^1U \leftarrow {}^1A$ transition is further shifted to about 1900 A. (5).

11. Thiocarbonyl compounds

McMurry (57) has given several references to earlier spectral studies of the thiocarbonyl group. Lewis and Kasha (47a) have performed additional studies. The absorption spectrum of thiophosgene (Cl$_2$CS) has been studied recently by Burnelle (17). Burnelle assigns the ^3U state near 15000 cm.$^{-1}$, and the ^1U state near 17500 cm.$^{-1}$ The $^1U \leftarrow {}^1A$ transition shows a 300 cm.$^{-1}$ blue shift in a solution of thiophosgene in acetone compared to a solution in hexane. The oscillator strength of the $^1U \leftarrow {}^1A$ transition is $f = 1.3 \times 10^{-4}$. Other bands have been observed at higher frequencies.

The oscillator strength of the $^1U \leftarrow {}^1A$ band and the separation between the ^3U and ^1U states of thiophosgene are remarkably similar to the corresponding transitions and states of formaldehyde. The lower energy of the $U \leftarrow A$ transition

of the   C=S group compared to the   C=O group is due to the lower ionization

potential of the $3p$ sulfur electrons compared to the $2p$ oxygen electrons (58).

F. STERIC EFFECTS IN $U \leftarrow A$ TRANSITIONS OF CARBONYL COMPOUNDS

In a series of papers, Leonard and coworkers have studied the ultraviolet absorption spectra of hindered benzils (45). In ordinary benzil (C$_6$H$_5$COCOC$_6$H$_5$) the longest-wave length $^1U \leftarrow {}^1A$ absorption maximum is at 3700 A. in solution in 95 per cent ethanol. This and other evidence is consistent with the skew structure of benzil in which the two benzoyl units lie in planes approximately at right angles to each other and in which the dicarbonyl system is not planar (47). The $^1U \leftarrow {}^1A$ dicarbonyl absorption maximum is shifted to longer wavelength with increasing hindrance at the ortho carbons of benzil, corresponding to increasing tendency for coplanarity of the two carbonyl groups. Other absorption maxima are simultaneously altered in wavelength and/or in intensity.

In another paper, Leonard and Mader (46) have studied the influence of steric configuration on the $^1U \leftarrow {}^1A$ bands in 1,2-diketones. In a series of α-diketones, the lowest $^1U \leftarrow {}^1A$ band shifts to shorter wavelengths as the angle between the carbonyl groups increases from 0°, in α-diketones, to larger angles in sterically hindered α-diketones. The $^1U \leftarrow {}^1A$ band moves toward shorter wavelengths as the angle increases from 0° to about 90°, and then shifts back again toward longer wavelengths as the angle increases beyond 90° with the dicarbonyl groups approaching a coplanar trans configuration (180° angle).

Cookson and Lewin (19) have observed a remarkable enhancement of the intensity of the $^1U \leftarrow {}^1A$ band of the dicarbonyl group and the carbonyl group in several compounds. The intensity of the $^1U \leftarrow {}^1A$ band is increased by a factor of 10 to 50 when the carbonyl or dicarbonyl group is in a molecule which contains phenyl groups or ethylenic groups which are not coplanar with the $>C{=}O$ or $O{=}C{-}C{=}O$ group. This effect appears even when the carbonyl group is not directly conjugated with the phenyl or ethylenic group. This type of spectroscopic interaction between unconjugated chromophores has been discussed by Cookson and Wariyar (20), who also give numerous references to previous work in this field. They suggest that the $^1U \leftarrow {}^1A$ carbonyl band near 2900 A. is abnormally intense only when the p_π orbitals of $C^{(1)}$ and $C^{(3)}$ in the system,

$$O{=}C^{(1)}{-}C^{(2)}{-}C^{(3)}{=}C^{(4)}$$
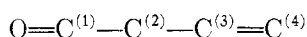
point directly at one another. The detailed explanation of this important phenomenon is not understood.

G. $W \leftarrow A$ AND $U \leftarrow A$ TRANSITIONS IN AZA-AROMATIC COMPOUNDS

1. Pyridine (azabenzene)

The absorption bands of gaseous pyridine in the region 3000-2500 A. were first observed by Henri and Angenot (32). Sponer and Stuecklen (99) reëxamined these bands and proposed a vibrational analysis. Subsequently, Sponer and Rush (98) compared the spectra of pyridine and the methylpyridines (picolines). They suggested that there are two distinct electronic transitions in the 3000–2450 A. region. One transition consists of sharp bands from 3000 A. to 2700 A. This transition is overlapped at its short-wavelength end by a stronger transition, which consists of broad bands from 2700 A. to 2450 A. At that time, Sponer and Rush thought that both of these transitions were $\pi \to \pi^*$. However, in a subsequent paper (86), Rush and Sponer concluded that the weak, sharp bands of pyridine near 35500 cm.$^{-1}$ are due to the $n_N \to \pi^*$ transition, $^1B_2 \leftarrow {}^1A_1$, while the stronger, broad bands near 38500 cm.$^{-1}$ are due to the $\pi \to \pi^*$ transition, $^1B_1 \leftarrow {}^1A_1$. Rush and Sponer assigned the band at 34769 cm.$^{-1}$ to the 0–0 band of the $n_N \to \pi^*$ transition in pyridine. The 0–0 band of the $\pi \to \pi^*$ transition was not identified with certainty, but was assigned to one of the bands near 38350 cm.$^{-1}$.

Stephenson (100) has studied the $n_N \to \pi^*$ transitions in substituted pyridines. He estimates the oscillator strength to be $f \cong 0.003$ for the $n \to \pi^*$ transition and $f = 0.05$ for the $\pi \to \pi^*$ transition in pyridine. The $n_N \to \pi^*$ transition cannot be clearly identified in the spectra of 2-X-pyridine (X = F, Cl, or Br), and Stephenson concludes that it is shifted to shorter wavelengths and is hidden by the stronger $\pi \to \pi^*$ transition. Stephenson interprets this as a result of lowering of the energy of the n_N orbital by the electron-attracting inductive effect of the halogen substituent. Other workers have suggested that the intramolecular blue shift is due to the electron-donating resonance effect of the halogen substituent which increases the energy of the excited state relative to the energy of the ground state. Measurement of the ionization potential of an electron in the n orbital in these molecules would provide a means of distinguishing between the

two alternative interpretations of the intramolecular blue shift. It is possible that both mechanisms might be important.

Reid (82) has observed some very weak absorption bands in pyridine near 31000 cm.$^{-1}$ These have been shown by Brealey (13) to be due to a trace of pyrazine impurity. The 26000 cm.$^{-1}$ phosphorescence of pyridine is also due to the pyrazine impurity (13).

Very recently, Evans (24) has observed what appears to be a *bona fide* singlet-triplet transition in pyridine near 30000 cm.$^{-1}$, using dissolved paramagnetic oxygen to perturb the electronic states of pyridine and cause an increase in the intensity of the spin-forbidden transition. Evans tentatively concludes that the singlet-triplet transition is $\pi \rightarrow \pi^*$, probably $^3L_a \leftarrow {}^1A$ by analogy with benzene.
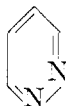
It should be mentioned that the $n_N \rightarrow \pi^*$ transition in pyridine possesses both $^1W \leftarrow {}^1A$ and $^1U \leftarrow {}^1A$ character if the π^* orbital has a nonvanishing amplitude at the nitrogen atom, assuming that the n_N orbital is approximately an sp^2 hybrid orbital. On the other hand, if the π^* orbital has no amplitude at the nitrogen atom, the $n_N \rightarrow \pi^*$ transition possesses no $^1W \leftarrow {}^1A$ character and should be much weaker. The oscillator strength for the $n_N \rightarrow \pi^*$ transition in pyridine ($f \cong 3 \times 10^{-3}$) suggests that there may be a significant amount of $^1W \leftarrow {}^1A$ character in this transition.

2. The diazabenzenes

Halverson and Hirt (30) have studied the spectra of pyridine, pyridazine,

Pyridine   Pyridazine   Pyrimidine   Pyrazine

pyrimidine, and pyrazine in hydrocarbon solvents and in hydroxylic solvents. They have shown which transitions are $n \rightarrow \pi^*$, $^1W \leftarrow {}^1A$, and which transitions are $\pi \rightarrow \pi^*$. They have also studied the spectra of various halo-substituted pyrazines and pyridazines. The lowest $n \rightarrow \pi^*$, $^1W \leftarrow {}^1A$ transition is near 30000–35000 cm.$^{-1}$, and the lowest $\pi \rightarrow \pi^*$ transition is near 38000–41000 cm.$^{-1}$ The effects of hydroxylic solvent and halogen substituent on the $^1W \leftarrow {}^1A$ transition are quite pronounced. The vapor spectra of the diazabenzenes have also been studied by Halverson and Hirt (29).

More recently, Ito, Shimada, Kuraishi, and Mizushima (42) have analyzed the absorption bands of gaseous pyrazine near 3200 A. Under fairly high resolution, it is possible to distinguish two types of band systems in the absorption spectrum. One system consists of sharp bands which degrade to longer wavelengths. This system is assigned to a $^1W \leftarrow {}^1A$ transition which is allowed by molecular symmetry, $^1B_{1u} \leftarrow {}^1A_g$, with 0–0 band at 30875 cm.$^{-1}$ Prominent progressions of an upper-state vibrational frequency of 584 cm.$^{-1}$ appear in the spectrum. The corresponding vibrational frequency in the lower state is 600 cm.$^{-1}$ The second absorption band system consists of broader bands which de-

grade to shorter wavelengths. This system is weaker than the sharp system. It is assigned to a $^1W \leftarrow {}^1A$ transition which is forbidden by molecular symmetry, $^1B_{3g} \leftarrow {}^1A_g$. Vibrational frequencies of 561 cm.$^{-1}$ (upper state) and 600 cm.$^{-1}$ (lower state) are prominent in this transition. The 0–0 band is estimated to be between 30545 cm.$^{-1}$ and 31260 cm.$^{-1}$ Two $n_N \rightarrow \pi^*$, $^1W \leftarrow {}^1A$ transitions are expected in these diazabenzene compounds.

3. The triazabenzenes

The ultraviolet absorption spectrum of s-triazine

has been observed by Hirt, Halverson, and Schmitt (36). The bands of the $^1W \leftarrow {}^1A$ transition in gaseous s-triazine are sharp, although a vibrational analysis has not yet been proposed. The lowest $^1W \leftarrow {}^1A$ transition shows an absorption maximum near 36800 cm.$^{-1}$ in solution in a hydrocarbon solvent. The solvent blue shift and the intramolecular blue shift (blue shift due to electron-donating substituents) have also been studied.

The compound 3-amino-1,2,4-as-triazine shows a $^1W \leftarrow {}^1A$ transition with $\epsilon_{max} \cong 500$, $\nu_{max} \cong 26000$ cm.$^{-1}$ The blue shifts have also been studied (38).

### 4. The tetraazabenzenes

It has long been known that s-tetrazine,

possesses an absorption band in the visible region of the spectrum, between 5570 A. and 4980 A. It is known that $\epsilon_{max} \cong 660$ in solution (49). Compared to the diazabenzenes, the energy of this transition is remarkably low.
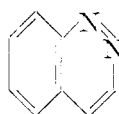
5. The azanaphthalenes

Hirt, King, and Cavagnol (37) have reported the spectra of a number of diazanaphthalenes, including studies of the solvent blue shift and the intramolecular blue shift. The $^1W \leftarrow {}^1A$ transition is near 27000 cm.$^{-1}$ in phthalazine,
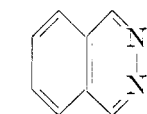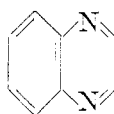
Phthalazine   Quinoxaline   Cinnoline

near 28000 cm.$^{-1}$ in quinoxaline, and near 26000 cm.$^{-1}$ in cinnoline. The lowest $\pi \rightarrow \pi^*$ transition is near 32000 cm.$^{-1}$ in these molecules, similar to naphthalene.

The second and third naphthalene-like $\pi \to \pi^*$ transitions have also been identified in some cases.

6. Azo compounds (—N=N—)

The absorption spectra of azobenzene ($C_6H_5N=NC_6H_5$) and numerous derivatives in ethanolic solution have been studied by Birnbaum, Linford, and Style (6). The azo group shows an absorption band near 4500 A. in both trans- and cis-azobenzene derivatives. The intensity in the cis isomer is greater than in the trans isomer. The oscillator strengths are approximately 1.6×10^{-2} for trans-azobenzene and 2.5×10^{-2} for cis-azobenzene. The oscillator strengths indicate that the transition is $^1W \leftarrow {}^1A$. The spectra show no trace of structure in the vapor phase.

H. $W \leftarrow A$ AND $U \leftarrow A$ TRANSITIONS IN MOLECULES CONTAINING NITROGEN–OXYGEN BONDS

1. Nitroso compounds

Orgel (66) has discussed the $^1U \leftarrow {}^1A$ transition of the nitroso group near 7000 A. Nakamoto and Suzuki (62) and Fenimore (24a) have shown that the weak band of the —N=O group in m-nitronitrosobenzene
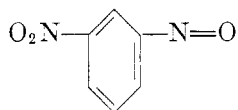
($\lambda_{max} = 7600$ A.) possesses a transition moment which is perpendicular to the plane of the benzene ring. This is in agreement with theoretical predictions based on the simple molecular orbital theory. The work of Nakamoto and Suzuki and of Fenimore is based on a study of the polarized absorption spectra of single crystals and single mixed crystals of m-nitronitrosobenzene.

Recently, Mrs. J. Mason (51) has measured and discussed the $n \to \pi^*$ transition in CF_3NO and in related compounds. The oscillator strength is $f \cong 2 \times 10^{-4}$. Her assignment is $n_N \to \pi^*$, $^1W \leftarrow {}^1A$. However, the intensity is similar to that for the $^1U \leftarrow {}^1A$ transition in carbonyl compounds. The assignment $n_O \to \pi^*$, $^1U \leftarrow {}^1A$ is therefore more likely, in this author's opinion.

2. Nitrite compounds (RONO) and nitro compounds (RNO₂)

The long-wavelength bands of alkyl nitrites in the region from 25000 cm.$^{-1}$ to 30000 cm.$^{-1}$ have been studied by several authors. Elkins and Kuhn (23) find evidence for two different electronic transitions in this region, based on the variation of the circular dichroism and anisotropic factor of optically active alkyl nitrites. According to Tarte (101) and d'Or (65), such a hypothesis would explain the anomalies in the vibrational structure in the electronic spectra of alkyl nitrites and nitrous acid. The $n_O \to \pi^*$, $^1U \leftarrow {}^1A$ transition is almost certainly responsible for the major part of the intensity in the long-wavelength region of the alkyl nitrites.

The weak, long-wavelength bands of CF_3NO_2 appear at 36000 cm.$^{-1}$ with $\epsilon_{max} \cong 11.2$ (51). The $n_O \rightarrow \pi^*$, $^1U \leftarrow {}^1A$ assignment is consistent with the low intensity of this transition.

Phosphorescence spectra of several nitro compounds are known (47a).

3. Molecules and molecule-ions, XO_y^{z-}, including the nitrite ion

McGlynn and Kasha (55) have reviewed the literature data pertaining to the absorption spectra of molecules and molecule-ions of the type XO_y^{z-}. They predict that many inorganic molecules containing oxygen should exhibit an $n \rightarrow \pi^*$ transition as the transition of longest wavelength. They have also tried to correlate weak absorption bands ($\epsilon_{max} < 50$) with transitions which are forbidden by molecular symmetry, and stronger absorption bands ($\epsilon_{max} > 1000$) with transitions which are allowed by molecular symmetry. However, in at least one case, it has been shown that McGlynn and Kasha's simple treatment fails to predict the correct assignment. Trawick and Eberhardt (102) and, more recently, Sidman (94) have studied the spectra of nitrite ion in crystalline sodium nitrite. The longest-wavelength transition, $\lambda_{max} \sim 3550$ A., $\epsilon_{max} \sim 20$, is quite weak, but is definitely allowed by molecular symmetry, with a transition moment which is perpendicular to the plane of the nitrite ion. Sidman has also discussed the vibrational frequencies of nitrite ion in the ground state and in the lowest excited state (94).

According to Orgel (66), the lowest transition of nitrite ion is related to the lowest transition in RN=O. The large shift (~ 15000 cm.$^{-1}$) to higher frequencies is attributed to the electron-donating character of oxygen relative to R (R = C_6H_5 or CH_3). The low intensity of the long-wavelength transition in NO_2^-, RN=O, and RONO suggests that the transition is $^1U \leftarrow {}^1A$ in all three cases. If so, it must be $n_O \rightarrow \pi^*$ in nitrite ion rather than $n_N \rightarrow \pi^*$ as Trawick and Eberhardt (102) and Sidman (94) have previously suggested.

4. Pyridine N-oxide

A transition in pyridine N-oxide
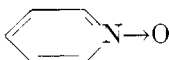
has been assigned as $n_O \rightarrow \pi^*$, $^1U \leftarrow {}^1A$ by Ito and Hata (40). The $^1U \leftarrow {}^1A$ absorption transition near 31500 cm.$^{-1}$ in a hexane solution is superimposed on the tail of a much stronger transition with absorption maximum at 35200 cm.$^{-1}$ The oscillator strengths have been estimated as $f \cong 0.012$ for the weaker transition and $f \cong 0.173$ for the stronger transition. Compared with the oscillator strength, $f \cong 10^{-4}$, for the $^1U \leftarrow {}^1A$ transition in carbonyl compounds, the value $f \cong 10^{-2}$ is abnormally high and is not consistent with a $^1U \leftarrow {}^1A$ assignment. The intense peak shifts very strongly to *shorter* wavelengths in ethanol and in water. The shift from the maximum in the hexane solution is approximately +2000 cm.$^{-1}$ in ethanol and +5000 cm.$^{-1}$ in water. The weaker bands which appear in the hexane solution cannot be identified in the spectra of solutions in

ethanol or in water. It therefore appears that the weaker transition shows an even larger blue shift than the stronger transition. Pronounced blue shifts of $\pi \to \pi^*$ transitions in solvents of high polarity are known to occur in the mero-cyanine dyes (15). The large blue shift is expected in polar solvents if the dipole moment decreases as a result of the electronic transition (54). Ito and Hata assign the strong transition as $\pi \to \pi^*$. The weaker transition may also be $\pi \to \pi^*$, in this author's opinion.

In another paper, Ito and Mizushima (41) have given a partial vibrational analysis of the longest-wavelength absorption transition of gaseous pyridine N-oxide. They conclude that the transition is allowed by molecular symmetry. Lacking fluorescence data, the analysis of the vapor absorption spectrum alone cannot eliminate the possibility that the transition may be forbidden by molecular symmetry. The spectrum of pyridine N-oxide will require further study.

III. SUMMARY AND CONCLUSIONS

At the present time, it is probably safe to say that we possess a good qualita-tive and semiquantitative understanding of electronic transitions in polyatomic molecules. In the domain of U—A transitions, the simple LCAO-MO picture gives a useful qualitative description of the low energy and low intensity of $^1U \leftarrow {}^1A$ transitions and the relatively small (about 0.4 e.v.) singlet-triplet separation between the ^3U and the ^1U states. The semiempirical methods appear to be useful for calculating semiquantitatively the energies of excited electronic states of carbonyl compounds, and further extension to other molecules appears desirable. More refined calculations would also be welcomed. The long-wave-length absorption and fluorescence spectra of formaldehyde are now well under-stood in their broad outlines, and additional high-resolution work should further clarify the details of molecular geometry and potential energy surfaces in the excited state. Further studies, both theoretical and experimental, of the excited triplet states should also prove interesting. Many features of the spectra of con-jugated carbonyl compounds are fairly well understood, but there is ample room here for further study.

Solvent effects have been successfully used to characterize $^1U \leftarrow {}^1A$ and $^1W \leftarrow {}^1A$ transitions. It should also be possible to study molecular interactions in more detail by this technique.

The $^1W \leftarrow {}^1A$ transitions in aza-aromatic compounds are worthy of additional studies. It would be particularly interesting to observe the ^3W—^1A transitions in absorption and/or phosphorescence.

Continued studies of the electronic spectra of small molecules and molecule-ions should be pursued. It is hoped that refined theoretical calculations might be carried out in the not too distant future for these relatively simple systems. If so, detailed spectroscopic investigations will be needed to provide data for com-parison with theoretical predictions.

In a review article of this scope, no effort has been made to cover every single reference dealing with $n \to \pi^*$ transitions. By way of summary, some of

TABLE 1

General features of $n \rightarrow \pi^*$ transitions and a comparison with $\pi \rightarrow \pi^*$ transitions

	$n \rightarrow \pi^*$ Transition	$\pi \rightarrow \pi^*$ Transition
Wavelength	See table 2	1500 A. to 10,000 A., depending on the system
Oscillator strength, f, and maximum molar extinction coefficient, ϵ_{max}	$^1W \leftarrow {}^1A : f \cong 10^{-2}$ ($\epsilon_{max} \cong 10^3$) $^1U \leftarrow {}^1A : f \cong 10^{-4}$ ($\epsilon_{max} \cong 10^1$) $^3W \leftarrow {}^1A : f = ?$ $^3U \leftarrow {}^1A : f \cong 10^{-6}$ ($\epsilon_{max} \cong 10^{-1}$)	$^1B_b \leftarrow {}^1A : f \cong 10$: ($\epsilon_{max} \cong 10^5$) $^1L_a \leftarrow {}^1A : f \cong 10^{-0.8}$ ($\epsilon_{max} \cong 10^4$) $^1L_b \leftarrow {}^1A : f \cong 10^{-2.5}$ ($\epsilon_{max} \cong 10^{2.5}$) $^3L_a \leftarrow {}^1A : f < 10^{-8}$ ($\epsilon_{max} < 10^{-3}$)
Vibrational structure	Often very sharp in vapor; less sharp in hexane solution; broad and structureless in alcohol or water solution, owing to hydrogen bonding.	Often moderately sharp in vapor and very sharp in mixed crystals at low temperature; moderately sharp in hexane or in alcohol solution.
Natural fluorescence lifetime and quantum yield (26)	The $^1U \rightarrow {}^1A$ fluorescence transition occurs in formaldehyde, glyoxal, biacetyl (weakly), acetone (weakly), and nitrite ion (weakly). The molecule is sometimes, though not invariably, nonfluorescent if an $n \rightarrow \pi^*$ transition is the lowest transition. No general rules can be given. $\tau \cong 10^{-5}$ sec. (calculated).	Most molecules having a $\pi \rightarrow \pi^*$ transition as the lowest transition will fluoresce. $\tau \cong 10^{-9}$ sec. to 10^{-6} sec. Quantum yields between 0.05 and 0.5 are often observed.
Natural phosphorescence lifetime and quantum yield (26)	The $^3U \rightarrow {}^1A$ phosphorescence transition sometimes occurs *in the vapor phase*, as well as in rigid glass at low temperature. $\tau \cong 10^{-2}$ sec. Quantum yields of 0.05 to 0.5 are often observed.	Most molecules having a $\pi \rightarrow \pi^*$ transition as the lowest transition will phosphoresce in a rigid glass at low temperature but *not* in the vapor phase. $\tau \cong 10^1$ sec. Quantum yields between 0.05 and 0.5 are often observed.
Direction of transition moment	Necessarily *perpendicular* to the molecular plane for singlet-singlet transitions which are allowed by molecular symmetry. Vibrational-electronic interaction may give bands with transition moment in the molecular plane.	Necessarily *in* the molecular plane for singlet-singlet transitions which are allowed by molecular symmetry. Vibrational-electronic interaction may give bands with a different direction of the transition moment.
Effect of polar solvent	Generally shifts to *shorter* wavelengths, owing to hydrogen bonding and/or to solvation of nonbonding electrons.	Generally shifts to *longer* wavelengths, owing to interaction of transition dipole with a polarizable medium. However, $\pi \rightarrow \pi^*$ transitions which shift to shorter wavelengths in a polar solvent are known to occur in certain heteropolar systems.
Effect of electron-donating substituents in the molecule	Shifts to *shorter* wavelengths, owing to increase in energy of the excited state caused by accumulation of electronic charge in a localized region.	Shifts to *longer* wavelengths, owing to resonance interaction between π-electron system and substituent. Weak transitions are enhanced, owing to the transition moment induced by asymmetric substitution.
Steric effects	Shifts to shorter wavelengths if steric effects decrease the length of the conjugated system. Intensity of $^1U \leftarrow {}^1A$ transitions in carbonyl compounds may increase as much as 100-fold in certain cases, owing to steric effects which are as yet unexplained.	Shifts to shorter wavelength if steric effects decrease the length of the conjugated system.

TABLE 2

Approximate wavelengths in Ångström units for $n \to \pi^*$ *absorption transitions*

The $^3U \leftarrow {}^1A$ transitions in the carbonyl compounds are about 3000 cm.$^{-1}$ lower in frequency than the corresponding $^1U \leftarrow {}^1A$ transition. The transitions are probably $^1U \leftarrow {}^1A$, except where $^1W \leftarrow {}^1A$ is indicated. Parentheses indicate estimates or hidden and unidentified transitions. The symbol X indicates that the group cannot go into a benzene ring. Question marks indicate doubtful assignment of observed bands. The table was compiled in part from reference 77.

Group	Group Alone (Alkyl-substituted)	Group On Vinyl	Group on Benzene Ring	Group on Benzene Ring
—CONH—	2000	(2400?)	X	(2700?)
—COOH	2100	2500	X	(2900?)
$\diagdown$C=N— $\diagup$	(2100?)	(2500?)	2900	(2900?)
--N=C—C=N—	—	(2500?)	3400 (^1W)	—
—NO$_2$	2700	2800	X	3300
—ONO$_2$	2700	—	X	—
$\diagdown$C=O $\diagup$	2800 (^1U); 1900 (^1W)	3200	X	3300
$\diagdown$N—N=O $\diagup$	3400	—	X	—
—N=N—	3700 (^1W)	—	3400 (^1W)	4000 (^1W)
—O—N=O	3700	—	X	—
—COCO—	4600 (^1U); 2800 (^1U)	—	4500 (*p*-quinone)	3700 (benzil, skew)
$\diagdown$C=S $\diagup$	5500	—	X	6000
--N=O	6800	—	X	7700

the characteristics of $n \to \pi^*$ transitions are discussed briefly in table 1, which is an extension of Kasha's characterization (44). The approximate wavelengths at which $U \leftarrow A$ and $W \leftarrow A$ transitions appear in several systems are given in table 2.

In conclusion, our understanding of the electronic spectra and structure of polyatomic molecules is now on much firmer ground than it was ten years ago. This has been due in part to the cooperation between theoreticians and experimentalists who have studied problems of mutual interest. As further work continues, it is possible that the electronic spectra of molecules eventually will be as well understood as the electronic spectra of atoms. Such a goal will provide both experimentalists and theoreticians with interesting work for several years to come.

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