Electronic Structures of Molecules X. Aldehydes, Ketones and Related Molecules

Robert S. Mulliken

For the eigenfunctions of these bands the energy has the same value for all values of **k**.

Although not very much of a quantitative nature can be concluded from these results, the essential differences between diamond and the metals are apparent. In a metal there is always an energy band which is not completely filled. As the various workers on metals have shown, the electrical conductivity is a direct consequence of this fact. In the diamond the low energy bands are all completely filled, and a large amount of energy would be necessary to promote an electron to an unfilled band. Now in each band, for every electron wave traveling in one direction there is a second wave of the same energy traveling in the opposite direction. The net result is that a filled band can produce no flow of charge. Hence it follows that the diamond is a nonconductor.

Some conclusions can be drawn with respect to the absorption spectrum. At the normal internuclear distance the curve III has risen to such a high energy that transitions of electrons from the filled bands to the band lying above it would take more energy than the ionization potential of the normal carbon atom. It is almost certain that some band arising from the $3d$ level of the carbon atom will have a lower energy. If ultraviolet light is absorbed by diamond it is most probable that the transition which actually takes place is one to

such a level. Peter[8] has measured the absorption coefficient and refractive index of diamond down to 2260A. No absorption bands were found, but extrapolation of the dispersion curve indicates an absorption band in the neighborhood of 1750A, corresponding to an excitation energy of about 7 electron volts. This value seems too low for a transition to a $2p$ band, and therefore is almost certainly evidence of a low $3d$ band.

An interesting feature of the eigenfunctions of the diamond is the change in character of the eigenfunctions of the second lowest band as the internuclear distance is decreased. For large separations the eigenfunctions of this band are s-like in character, but after the point of intersection of curves III and IV (Fig. 2) has been passed the eigenfunctions have essentially the character of p functions. This change in character is essentially· the promotion which Heitler and London have postulated to account for the quadrivalence of carbon. There is, however, no sign of the combination of s and p eigenfunctions into the "tetrahedral" eigenfunctions postulated by Slater and Pauling to account for the phenomena of directed valence observed in carbon.

The author wishes to express his deep appreciation to Professor J. C. Slater for his assistance and discussions of this problem.

---

[8] Peter, Zeits. f. Physik **15**, 358 (1923).

Electronic Structures of Molecules
X. Aldehydes, Ketones and Related Molecules

ROBERT S. MULLIKEN, *Ryerson Physical Laboratory, University of Chicago*
(Received June 22, 1935)

Electron configurations for the normal states of H_2CO, CH_3HCO, Cl_2CO are explicitly given, also for the low excited states of H_2CO. The structures, ionization potentials, and longest wavelength electronic band spectra of these and other related or analogous molecules (saturated aldehydes, ketones, thioaldehydes, thioketones, etc.) are interpreted in relation to these configurations. In particular is it shown that the minimum ionization potential of $\diagup\hspace{-0.4em}\diagdown C = O$ or $\diagup\hspace{-0.4em}\diagdown C = S$ corresponds to removal of a nonbonding $2p$ electron from the O atom or a nonbonding $3p$ from the S atom, unless the groups attached to the C contain other unusually easily ionized electrons. Similarly, the longest wavelength band system, commonly attributed

to the $C=O$ (or $C=S$) double bond, corresponds to excitation of the nonbonding $2p_O$ or $3p_S$ to an excited orbital which is largely but probably not quite wholly localized in the $C=O$ or $C=S$ bond, and which has $C\leftrightarrow O$ or $C\leftrightarrow S$ antibonding power, i.e., loosens the bond somewhat. This excitation process is responsible for color in the $\diagup\hspace{-0.4em}\diagdown C = S$ compounds. The $C=O$ (or $C=S$) bond is a true double bond in the sense that the binding is effected essentially by two pairs of $C-O$ (or $C-S$) bonding electrons. The $C=O$ bond is essentially the same also in saturated monobasic acids RCOOH or at least in their esters.

1. NORMAL STATE AND IONIZATION POTENTIAL OF FORMALDEHYDE

THE aldehydes $RHC=O$ and the ketones $R'RC=O$ can be considered as derivatives of formaldehyde H_2CO ($R=$ alkyl radical, or derivative thereof). Various other molecules such as $Cl_2C=O$, $Cl_2C=S$, $RHCS$, R_2CS can also be considered as derivatives or analogs of H_2CO. Even organic acids $R(OH)C=O$ and the derivatives can to a considerable extent be forced into this category.

Common to the absorption spectra of all the aldehydes and ketones is a band system near $\lambda 2900$, often showing fine structure. This is generally agreed to be associated with the presence of the $C=O$ bond. A second, much more intense, absorption system appears near $\lambda 1900$ in all aldehydes and ketones, except formaldehyde where it is apparently displaced to about $\lambda 1600$ or $\lambda 1700$. This second system seems also to be definitely associated with the presence of the

$C=O$ bond, as was pointed out to the writer by Dr. C. P. Snow in correspondence.

Except possibly in respect to the anomaly in the second system, formaldehyde may reasonably be taken as prototype for the aldehydes and ketones. In seeking to predict its electronic structure, we may note that it is isoelectronic with, and in a sense is intermediate between, $O=O$ and $H_2C=CH_2$, just as, e.g., CH_3I stands between I_2 and C_2H_6, or CH_3NH_2 between N_2H_4 and C_2H_6 (cf. earlier papers[1, 2]). As regards symmetry, $H_2C=O$ (symmetry C_{2v}) is closer to C_2H_4 (symmetry V_h) than to O_2 (symmetry $D_{\infty d}$), but inferior to both. Strong polarity is to be expected in the CO bond, and distinctly weaker polarities in the $C-H$ bonds.

On due consideration, taking cognizance of what is known (see below) about the ultraviolet spectrum and I (the ionization potential), one arrives at the following electronic structure (1s electrons of C and O are omitted):

$$(2s)^2[sa_1]^2[x_O+x_C, b_1]^2[yb_2]^2[z_O+z_{CH_2}, a_1]^2(2p_yb_2)^2, {}^1A_1.$$

approx. loc.	OH_2Co	$O-C$	CH_2	$O-CH_2$	O	
vert. I	(32) (22)	(15.5)	(15.5) (15?)	11		(1)

The I values in parentheses are *estimated* values, the other is observed. Axes z, x, y, are, respectively, along the symmetry axis, perpendicular to the plane of the molecule, and in the latter perpendicular to the symmetry axis. The $2s$ and $2p_y$ orbitals are, probably to a good approximation, nonbonding O atom orbitals. All the other orbitals have either $C-O$ or $C-H$ bonding properties, or both.

Configuration (1) is similar to the normal state configuration[2] of C_2H_4, except that one CH_2 group with its intraradical[1] orbital $[yb_2]$ have been replaced by the O atom with its nonbonding orbital $2p_yb_2$. The orbital $[x_O+x_C]$ here corresponds to $[x+x]$ in C_2H_4, and is strictly confined to the $C-O$ bond, just as $[x+x]$ is to the $C-C$ bond. It differs from the latter in being strongly polar, i.e., $[x_O+x_C]$ really means, in LCAO approximation,[3]

$$a(2p_x)_O+b(2p_x)_C,$$

with $a>b$ rather strongly, since O is much more electronegative than $2p_C$.[4]

The orbitals $(2s)$, $[s]$, and $[z_O+z_{CH_2}]$ here (all of type a_1) correspond to $[s+s, a_{1g}]$, $[s-s, b_{1u}]$, and $[\sigma+\sigma, a_{1g}]$ of C_2H_4 (z here means $2p_z$, as does σ for C_2H_4). There is, however, not a one to one correspondence. All that is definitely obvious about the forms of $(2s)$, $[s]$ and $[z_O+z_{CH_2}]$ is that in LCAO approximation they represent three of the four solutions of a perturbation problem starting from $2s_O$, $[s]_{CH_2}$, $(2p_z)_O$ and $[z]_{CH_2}$. Roughly, since the effective term value[4] of unperturbed $2s_O$ is much larger than that of $[s]_{CH_2}$, etc., the lowest-energy solution is just $2s_O$, as is indicated in (1). The orbital of next lowest energy is probably one built primarily on $[s]_{CH_2}$ but with a considerable admixture of $(2p_z)_O$, together with more or less of $[z]_{CH_2}$ and $(2s)_O$; this mixture is designated simply $[s]$ in (1). Its bonding power should be more or less divided between $C-H$ and $C-O$

[1] R. S. Mulliken, J. Chem. Phys. 3, 506 (1935): VII of this series.
[2] R. S. Mulliken, J. Chem. Phys. 3, 517 (1935): IX.
[3] R. S. Mulliken, J. Chem. Phys. 3, 375 (1935): VI.

[4] R. S. Mulliken, J. Chem. Phys. 3 (1935): XI, XII, the following articles.

bonding. The third solution, designated $[z_0+z_{CH_2}]$ in (1), probably is built mainly of $(2p_z)_O$ and $[z]_{CH_2}$ with the former probably more or less predominant, and probably gives fairly strong $C-O$ bonding combined with some $C-H$ bonding. A fourth solution, corresponding to an excited orbital which we shall encounter below under the designation $[z_{CH_2}-z_O, a_1]$, probably gives rather strong $C-O$ antibonding and some $C-H$ bonding (or possibly $C-H$ antibonding). Very roughly, it seems likely, we may take $[z_0+z_{CH_2}]$ and $[z_{CH_2}-z_O]$ as solutions of a simpler perturbation problem starting from $(2p_z)_O$ and $[z]_{CH_2}$, thus isolating them from $(2s)_O$ and $[s]$. The foregoing statements in regard to the forms of the a_1 orbitals, while probably roughly correct, cannot be counted on as entirely reliable without more careful consideration.

For this reason, the estimated I's for these orbitals are less certain than for the others. The estimated I's given in (1) are based on the usual methods,[5] with $I°=17.17$ volts, $I*=14.73$ volts as $2p$ comparison I's of the O atom, and $I°=11.21$ volts for $2p$ of the carbon atom. The estimated I for $[x_O+x_C]$ is obtained as follows:

$$I > \tfrac{1}{2}\{I°(2p_O)+I°(2p_C)\},$$

which gives $I>14.2$, say I about 17.5, since I should be at least as large as $I°(2p_O)$. Allowance for the fact that the O atom has a considerable net negative charge reduces the estimate[5] to perhaps about 15.5 volts.

The predicted I for the nonbonding orbital $(2p_yb_2)_O$ is simply $I*=14.73$ volts if no allowance is made for net charge on the O atom. If the charge on the O atom should prove to be about the same as in H_2O, as seems possible, although available electronegativity data[4] are not applicable here, we might expect the actual I to be reduced to about 12.7 volts as in H_2O, or lower (see below). Thus the minimum vertical I of H_2CO should without much doubt be the I for removal of a $(2p_y)_O$ electron.

The estimated I for $[yb_2]$ of the CH_2 radical is based on the idea that, as was likewise supposed for $[y]$ in C_2H_4, it is very similar to the y component of $[\pi]$ of the CH_3 radical in CH_3X or CH_4. The estimate given is somewhat larger than the $I=14.4$ volts of $[\pi]$ in CH_4, since the CH_2

group here is more positively charged because of the presence of the strongly negative O atom in the molecule. Interaction with $(2p_yb_2)_O$ should also tend to increase I of $[yb_2]$, I of $(2p_y)_O$ being decreased at the same time; but these effects are probably not large.

In a recent paper by Eastwood and Snow,[5a] dealing with the ultraviolet bands and electronic structures of aldehydes and ketones, the authors refer to an electron configuration given by the writer in 1933–4 letters to Dr. Snow. This differed from (1) above in that $[y+y]^2[y-y]^2$ was written instead of $[yb_2]^2(2p_yb_2)^2$; in other words, strong resonance between $[y]$ of CH_2 and $2p_y$ of O was assumed. This seemed necessary at the time, since the predicted I was about 14.4 volts for $[y]$ of CH_2 and 14.73 volts $=I*(2p)$ for O. The writer was not quite satisfied with this conclusion in relation to the ultraviolet H_2CO bands, and publication was postponed. Price's recent work, leading to the realization of the importance of charge transfer effects,[5] also other evidence tending to indicate lack of strong resonance in certain analogous cases even in the presence of degeneracy,[5] cleared up the remaining doubts, and led to the present conclusion that there is not much interaction between $[y]$ of CH_2 and $(2p_y)$ of O, and that the latter has a considerably smaller I than the former, mainly because of charge-transfers. Nevertheless there must be *some* interaction and mixing between the two orbitals, possibly enough to affect their I's appreciably.

The observed I_{min} of H_2CO is 11.3 ± 0.5 volts according to Jewitt (electron impact method), and 10.83 ± 0.1 volts according to Price (Rydberg series).[6] Although these values are considerably lower than that suggested above, there is practically no doubt that they must be identified with removal of $(2p_y)_O$; strong evidence supporting this is obtained from certain ultraviolet bands to be discussed below. A reasonable explanation of the low I is as follows: in H_2O the nonbonding analog $(2p_z)_O$ of the present $(2p_y)_C$ is in the field of the net negative charge on the O, but this field is partly compensated by the fields of the

[5] R. S. Mulliken, J. Chem. Phys. 3, 514 (1935): VIII.

[5a] E. Eastwood and C. P. Snow, Proc. Roy. Soc. A149, 434 (1935).
[6] T. N. Jewitt, Phys. Rev. 46, 616 (1934); W. C. Price, Phys. Rev. 46, 529 (1934), and private communication.

nearby positive charges on the H's. In H_2CO, assuming the same net negative charge on the O as in H_2O, the net lowering of I of $(2p_y)_O$ is greater because the corresponding positive charges, mostly on the H's but partly on the C, are now very considerably farther away. Possibly interaction with $[y]$ of CH_2 also has an appreciable part in making I low for $(2p_y)_O$.

2. Ultraviolet Bands of Formaldehyde and other Aldehydes and Ketones

Now we can proceed to the interpretation of the ultraviolet H_2CO bands near $\lambda 2900$.[5a, 7, 8, 9] Of especial importance is the rotational analysis[9] of several of the bands by Dieke and Kistiakowsky. This shows that the molecule still has the plane Y shape in the upper electron level, and that the three moments of inertia are all increased by amounts ranging from about 8 to 15 percent. From this it follows that the H−H distance is increased, but that the C−O distance is increased more in proportion; what has happened to the C−H distances is not determined.

The rotational analysis shows that, for the six bands investigated, including A, B, C of the main vibrational series ($\lambda\lambda 3520$, 3390, 3260), the electric moment of the transition vibrates in the y direction, i.e., in the plane of the molecule. The selection-polarization rules[10] for symmetry C_{2v} permit a y electric moment only for transitions $A_1 \longleftrightarrow B_2$ or $A_2 \longleftrightarrow B_1$. (Note that for symmetry C_{2v} the x, y, z components of electric moment belong, respectively, to the representations b_1, b_2 and a_1.)[10]

Now it must be recognized that we cannot in general assume that a y electric moment necessarily means a $B_2 \longleftrightarrow A_1$ or $A_2 \longleftrightarrow B_1$ *electronic* transition. Instead, the symbols A_1, B_2, A_2, B_1 refer in general to the *total* $e \times v$ (*electronic* $\times$ *vibrational*) state. Electronic, vibrational and

total $e \times v$ state are all classified according to representations of the group C_{2v}, and the representation to which the total $e \times v$ state belongs is the direct product of the representations to which the electronic and vibrational states separately belong.[10] For example, if the electronic state is $^1B_2$ and the vibrational state is A_2, the total $e \times v$ state is $^1B_2 \times ^1A_2 = ^1B_1$; similarly, $^1A_1 \times ^1A_1 = ^1A$; $^1A_1 \times B_1 = ^1B_1$, $^1B_2 \times A_1 = ^1B_2$, $^1B_2 \times B_1 = ^1A_2$; $^3B_2 \times B_1 = ^3A_2$; etc.[10]

In case we should know that the vibrational states involved are both totally symmetrical (i.e., type A_1), or at least both alike, for the upper and lower electron levels, *then* we could conclude from the observed y electric moment that the *electron* transition is either $A_1 \longleftrightarrow B_2$ or $B_1 \longleftrightarrow A_2$. There is, of course, no doubt that the lower electron level is of type $^1A_1$ (cf. Eq. (1)). Hence, if only symmetrical vibrations are present for the bands analyzed, the upper electron level is B_2, doubtless $^1B_2$ since transitions to $^3B_2$, if present, should be much weaker than to an accompanying $^1B_2$. We must now consider two possibilities: (a) the electron transition is one allowed by the electronic selection rules; (b) it is one forbidden by these rules. The second possibility is of course unlikely, but nevertheless cannot be entirely ruled out, since the selection rules are rigorous only for the total $e \times v$ state, and only approximately so for the electronic and vibrational states separately.[11]

If (a) the electronic transition is an allowed one, then we can confidently conclude that the transition is $^1A_1 \longleftrightarrow ^1B_2$. For with an allowed electron transition, the strongest bands in the system, and all long series of strong bands, must conform to the Franck-Condon principle; now three of the bands analyzed belong to a long strong series which includes the strongest bands; and it can be seen that only symmetrical vibrations (type a_1, giving resultant vibrational states A_1) can be strongly excited without conflicting with the Franck-Condon principle.

We now seek to determine the electron configuration of the $^1B_2$ state indicated by the preceding discussion. Possible excited states which might have fairly low energy are

[7] V. Henri and S. A. Schou, Zeits. f. Physik **49**, 774 (1928). G. Herzberg, Trans. Faraday Soc. **27**, 378 (1931). Vibrational analysis.

[8] G. Herzberg and K. Franz, Zeits. f. Physik **76**, 720 (1932); S. Gradstein, Zeits. f. physik. Chemie **B22**, 384 (1933). Fluorescence.

[9] G. H. Dieke and G. B. Kistiakowsky, Proc. Nat. Acad. Sci. **18**, 367 (1932); Phys. Rev. **45**, 4 (1934). Rotational analysis.

[10] R. S. Mulliken, Phys. Rev. **43**, 279 (1933): IV. Cf. Table I, noting with care the last paragraph of "Explanation of Tables," which is rather condensed, and section 5. Or cf. A. Bushkovitch, Phys. Rev. **45**, 545 (1934).

[11] G. Herzberg and E. Teller, Zeits. f. physik. Chemie **B21**, 410 (1933).

$$(2p_y b_2)^{-1}[x_C - x_0, b_1], \; ^{1, 3}A_2; \; (2p_y b_2)^{-1}[z_{CH_2} - z_0, a_1], \; ^{1, 3}B_2;$$
$$[x+x, b_1]^{-1}[x-x, b_1], \; ^{1, 3}A_1; \; [x+x, b_1]^{-1}[z-z, a_1], \; ^{1, 3}B_1;$$
$$[z+z, a_1]^{-1}[x-x, b_1], \; ^{1, 3}B_1; \; [z+z, a_1]^{-1}[z-z, a_1], \; ^{1, 3}A_1; \qquad (2)$$
$$[y b_2]^{-1}[x-x, b_1], \; ^{1, 3}A_2; \; [y b_2]^{-1}[z-z, a_1], \; ^{1, 3}B_2;$$

and another set of states like those in the second column except for the substitution of $3s a_1$ for $[z_{CH_2} - z_0, a_1]$. Since we are looking for a $^1B_2$ upper level, our attention centers on the states with configurations $(2p_y b_2)^{-1}[a_1]$ and $[y b_2]^{-1}[a_1]$, where $[a_1]$ may be $[z-z, a_1]$ or $3s a_1$. As between $[y b_2]^{-1}$ and $(2p_y b_2)^{-1}$, the first can safely be dismissed in favor of the second, in view of our study of predicted and observed I values. Granting this, we have only to decide between the two possibilities for $[a_1]$.

In the band system near $\lambda 2900$, now under discussion, the first band starting from the vibrationless normal molecule (band· A) has a frequency corresponding to 3.5 volts, while the peak of intensity (near band F) corresponds to 4.2 volts. The latter may be taken as the approximate *vertical* excitation energy for the electron transition. On subtracting it from 11 volts, the approximate vertical I of the molecule, identified above with removal of $(2p_y b_2)$, we get about 6.8 volts as vertical term value for $[a_1]$. This value is surely too large for $3s a_1$, whether the latter is centered near the O atom or between the O and C.

This leaves $^1B_2$ of

$$(2p_y b_2)^{-1}(z_{CH_2} - z_0, a_1), \; ^{1, 3}B_2 \qquad (3)$$

as the probable upper level of the observed bands· An objection .nay be raised to this on the ground that in previous papers, especially IX,[2] the orbital $(z-z)$, e.g., in C_2H_2, C_2H_4 and C_2H_6, has been considered be to very high in energy, i.e., to have a term value even smaller than $3s$. In view of the strong polarity of the C$-$O bond here, however, $[z-z]$ here may well be very considerably different in term value than in more symmetrical molecules.

We come thus to the conclusion that, if the electron transition is an allowed one, there is little doubt that its upper level is $^1B_2$ of (3). It may be advisable, however, to consider the possibility that the electron transition is of forbidden type. The only possibility of this, since the normal state is surely $^1A_1$, is $^1A_1 \rightarrow ^1A_2$,

doubtless $^1A_1 \rightarrow ^1A_2$. This is, however, possible only if the transition for the total $e \times v$ state obeys the rigorous selection rules; furthermore, to agree with observation, the transition must give a y electric moment and so be either $A_1 \longleftrightarrow B_2$ or $A_2 \longleftrightarrow B_1$. Two likely ways in which these conditions could be satisfied for the observed bands are

$$(^1A_1 \times A_1 = ^1A_1) \rightarrow (^1A_2 \times B_1 = ^1B_2) \qquad (4a)$$
or
$$(^1A_1 \times B_1 = ^1B_1) \rightarrow (^1A_2 \times A_1 = ^1A_2). \qquad (4b)$$

In (4a), we may start from a nonvibrating molecule and end with a molecule in a vibrational state B_1, which could be obtained most šimply if one quantum of a mode of vibration of symmetry b_1 is excited, together with any number of quanta of symmetry a_1. In (4b), we start from a molecule having, in the simplest case, one quantum of b_1 type; (4b) would become more intense with rise in temperature. There is for H_2CO just one mode of vibration of symmetry b_1, namely, the mode in which the molecule bends out of its plane equilibrium form. This should have a very low frequency. Although its strong excitation, in (4a) especially, would be counter to the Franck-Condon principle, it seems quite possible that the necessary absorption (4a), or loss (4b), of one vibrational quantum of this mode might occur fairly readily.

As for the reason why a "forbidden" electronic transition could occur,[11] this can be explained as follows, taking (4a) as an example. The (4a) $e \times v$ levels of type $(^1A_2 \times B_1 = ^1B_2)$ may be perturbed by other $^1B_2$ $e \times v$ levels of the molecule, of type $^1B_2 \times A_1 = ^1B_2$, probably belonging to a higher-energy electron state. Since transitions to $(^1B_2 \times A_1 = ^1B_2)$ from the normal state $(^1A_1 \times A_1 = ^1A_1)$ are allowed by the electronic selection rules, transitions to $(^1A_2 \times B_1 = ^1B_2)$ will also occur weakly when the latter are perturbed by $(^1B_2 \times A_1 = ^1B_2)$. Some support is given to this sort of interpretation of the observed band system by the fact that it is much weaker than other systems further in the ultraviolet. In the deriva-

tives of H_2CO (aldehydes and ketones), the intensity ratio between the bands near $\lambda 2900$ and the next system near $\lambda 1900$ is about 1 : 300, according to a letter from Dr. C. P. Snow. This ratio is, however, really not so very large, and many other examples are known, in diatomic as well as polyatomic molecules, where long wavelength bands are very much weaker than shorter wavelength bands, even when there is no reason to believe that the electronic transition is barred by a selection rule. Hence the low intensity of the bands is not at all conclusive evidence of a forbidden electronic transition; if anything, the observed intensity is surprisingly high for such.

There is, however, one feature of the spectrum near $\lambda 3000$, not yet mentioned, which tends to favor the idea of a forbidden electron transition. The absorption spectrum contains a very weak band, called α, which does not fit in well with the others. It apparently comes from an excited vibrational state of the normal molecule, since it is reported[9] to be especially sensitive to temperature. Thus its weakness is partly explained, but there are other difficulties. Fluorescence can be excited in H_2CO by absorption of bands in the main system,[8] but apparently the actual fluorescence bands all start only from the upper level of α. It has been suggested[8] that the latter must be lower than the upper levels of any of the main bands, so that by collisions all molecules in higher levels are driven down to it before giving fluorescent radiation. In this case the upper level of α either must belong to a different electron state than for the other bands, or else the lowest upper vibrational state involved in the other bands is not one with all vibrational quantum numbers zero. The latter possibility could be understood if the lowest upper level observed in the other bands is of type $(^1A_2 \times A_1 = {}^1A_2)$. Transition to the latter from the normal, nonvibrating $(^1A_1 \times A_1 = {}^1A_1)$ state of the molecule would be rigorously forbidden, which would explain the fact that the upper level of band α can be reached only through absorption by already vibrating molecules (presumably of type $(^1A_1 \times B_1 = {}^1B_1)$, cf. $(4b)$).

The foregoing explanation would make α belong, with the other bands, to a forbidden electronic transition, with a $^1A_2$ upper electron level. If this is correct, there is for it one and only one acceptable electron configuration (cf. the possibilities in (2)), and this one entirely reasonable, namely

$$(2p_y b_2)^{-1}[x_C - x_O, b_1], {}^{1,3}A_2. \qquad (5)$$

This would make $[x - x]$ instead of $[z - z]$ the lowest excited orbital in H_2CO, which is reasonable and in accord with conclusions[2] in regard to C_2H_4 and O_2.

If the foregoing explanation of the α band, making the electron transition of forbidden type, is not correct, then it is probable that the α band has a different upper electron level than the other bands. This might possibly be $^3B_2$ of (3), but the temperature behavior of α and other evidence indicate that, if the other bands belong to an allowed electron transition, then α must belong to a forbidden one, probably that just suggested above for it. This would explain its *weakness;* its *presence* could be explained as a result of perturbation of its upper level $(^1A_2 \times A_1 = {}^1A_2)$ by levels of type $(^1B_2 \times B_1 = {}^1A_2)$ associated with the upper electron level of the other bands. If α belongs to a forbidden transition, the same reasoning used above leads clearly to $^1A_2$ of (5) as its upper electron level. In this case, we would have evidence of two excited electron levels, with $^1A_2$ of (5) a few tenths volt below $^1B_2$ of (3), and with $[x - x]$ slightly higher in I than $[z - z]$. The corresponding levels $^3A_2$ and $^3B_2$ would necessarily also exist, but bands to them would be very weak.

It will be noted that regardless of whether (3) or (5), or both, are the upper levels of the observed bands, our conclusion that $(2p_y)_0$ is the most easily ionized orbital in (1) receives confirmation, the possibilities $[x + x]$ and $[z + z]$ being directly ruled out by the y character of the electric moment, while $[y b_2]$ has been eliminated by other considerations. Thus we can conclude rather definitely that the electron transition involved in the bands is of the type
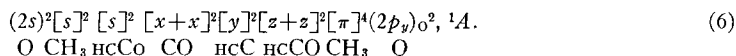
$$(2p_y)_0 \rightarrow [a - a],$$

where $[a - a]$ is a $C \longleftrightarrow O$ antibonding orbital, either $[z_{CH_2} - z_O]$ (probably) or $[x_C - x_O]$ (possibly).

This conclusion is in harmony with the effects of the transition on the moments of inertia.[9] These indicate, as noted above, that the $C - O$

distance is moderately increased, and that small or at most moderate changes occur in the HCH angle and CH distances. It also explains how, and in what sense, the transition is localized in the C=O bond; and it makes clear why an analogous band system, in very nearly the same wavelength region in all, is found in other saturated aldehydes RHCO and ketones RR′CO.

It may be helpful here to give electron configurations for CH_3HCO as a typical aldehyde and $(CH_3)_2CO$ as a typical ketone. For acetaldehyde we have, omitting $1s$ electrons:

$$(2s)^2[s]^2 \ [s]^2 \ [x+x]^2[y]^2[z+z]^2[\pi]^4(2p_y)_0^2, \ ^1A. \qquad (6)$$
$$\text{O } CH_3 \ _HCCo \ \ CO \ \ \ _HcC \ _HcCO \ CH_3 \ \ O$$

This is essentially the same as (1) except that the electrons $[s]^2[\pi]^4$ of the CH_3 group have been added, and except that in $[y]$, $[z+z]$, and the second $[s]$, the C of CO is bonded to one H and one C instead of to two H's as in H_2CO. No representation symbols have been used in (6), since strictly speaking there is no symmetry except for special and probably unimportant angles of rotation of the CH_3 group. Strictly speaking there is more or less interaction and mixing among all the various orbitals given in (6), also a splitting of $[\pi]$. Also there is some arbitrariness in using the CH_3 intraradical orbitals $[s]$ and $[\pi]$.

Nevertheless there are sufficient reasons for believing that the set of partially localized orbitals used in (6) constitutes a good approximation, corresponding well to observable I's with approximately correct localization of the "hole" in the electron density distribution produced by each I. (Cf. discussions in VII of this series[1] for further explanation.) Empirically, the similarity of the longer wavelength bands of H_2CO and CH_3HCO is satisfactory evidence that the orbitals involved in the C−O bond are nearly alike in H_2CO and CH_3HCO, so that (6) is a good approximation if (1) is. Farther in the ultraviolet, CH_3HCO should have bands and I's not found in H_2CO, namely, those corresponding to excitation of an electron from $[s]$ or $[\pi]$ of CH_3. The I's for these can be predicted to be approximately the same as for $[s]$ and $[\pi]$ of CH_3 in CH_4 or CH_3I. In practice, the spectrum of I's and of bands will tend to become perhaps hopelessly complicated at shorter wavelengths.

For $(CH_3)_2CO$ a configuration similar to (6) can be written, but with an $[s]$ and $[\pi]$ group for *each* CH_3. The observed I, as recently obtained by Noyes and Duncan[11a] (10.20 volts from a prob-

able Rydberg series, 10.1 volts from electron impact), is remarkably low, but must again be ascribed to $(2p_y)_0$.

In a recent paper,[5a] Eastwood and Snow have studied the changes in the longest wavelength bands in going from H_2CO to other aldehydes. On this basis they adduce empirical evidence (change of C−O vibration frequency of the upper electron level) which tends to favor $(2p_y)_0 \rightarrow [z-z]$ as against $(2p_y)_0 \rightarrow [x-x]$ for the electron transition involved. This evidence indicates lack of complete localization of the transition in the C−O bond, in agreement with $(2p_y)_0 \rightarrow [z-z]$.

In the shorter wavelength ends of the λ2900 band of H_2CO[7] and of analogous bands of the other aldehydes and ketones, marked predissociation occurs. The fact, demonstrated by Norrish,[12] that the predissociation in H_2CO gives H_2+CO, in RHCO gives $RH+CO$, and in RR′CO gives $RR'+CO$ (R = alkyl or substituted alkyl radical), has in the writer's opinion little, if any, direct dependence or bearing on the nature of the electron transition involved. The writer's view would be that the excited and vibrating molecule in each case simply predissociates into another electronic state whose n-dimensional potential energy surface is such that the molecule breaks up directly into CO plus H_2 or RH or RR′. There seems to be no need that the primary excitation process shall have any special loosening effect on the C−H or C−R bonds, as apparently it does not.

The absence or at least extreme slowness of predissociation from the upper level of the α band in H_2CO, shown by its ability to serve as upper level for fluorescence,[8] may be taken as evidence, although not conclusive, that the α band belongs to a different electron transition than the other bands.

[11a] A. B. F. Duncan, J. Chem. Phys. **3**, 131 (1935); W. A. Noyes, Jr., J. Chem. Phys. **3**, 430 (1935).

[12] R. W. G. Norrish and co-workers. cf. Trans. Faraday Soc. **30**, 108 (1934).

In concluding this section, we should mention the second ultraviolet system found in aldehydes and ketones, and attributed, like the first system, to a transition in the $C=O$ bond (cf. beginning of this paper). A number of possibilities for the upper state of these bands are included in (2) and in (2) modified by substituting $3sa_1$ for $[z-z, a_1]$. Transitions from the normal state to any of these, with the exception of those involving $[yb_2]^{-1}$, are localized more or less completely in the $C=O$ bond, and so would be capable of accounting for the occurrence of the bands in question with little modification in all aldehydes and ketones. The possibilities are so numerous, however, that it would be futile, without further knowledge of the band structure, to attempt to decide which one or ones correspond to the actual bands. (The fact[12] that absorption in this region does not cause predissociation to give CO seems to be of no particular help here.) Transitions from the normal state to all types except A_2 are allowed by the electronic selection rules, with electric moments x, y, z, respectively, for upper electron levels B_1, B_2 and A_1. It is probable, however, that many of the allowed transitions are very weak or are represented by continua rather than discrete bands.

3. OTHER MOLECULES CONTAINING $C=O$ AND $C=S$ BONDS

The characteristic absorption bands of the $C=O$ bond as found in aldehydes and ketones may reasonably be expected to occur also in other compounds of the general type $\begin{smallmatrix}A\\B\end{smallmatrix}\!\!>\!\!C=O$, while analogous bands are to be anticipated in $\begin{smallmatrix}A\\B\end{smallmatrix}\!\!>\!\!C=S$. Cases like $O=C=O$, $O=C=S$, $S=C$ $=S$, etc., where the symmetry is quite different, should not be expected to show bands corresponding in any close way to those of the $C=O$ and $C=S$ bonds in $ABC=O$ and $ABC=S$; they will be considered in XIV of this series.
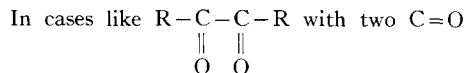
In cases like $R-C-C-R$ with two $C=O$ bonds close together, the beginning of absorption is observed to be displaced toward longer wavelengths. This is apparently a result of some kind of strong interaction within the $O=C-C=O$ system of bonds. These and other similar cases[12a] will, however, not be considered in this paper.

A few examples of the types $ABC=O$ and $ABC=S$ will now be taken up. In the important molecule phosgene, $O=CCl_2$, which has symmetry C_{2v} just like H_2CO, the two H atoms of H_2CO are replaced by Cl atoms. The electron configuration should be qualitatively the same as (1), except for the addition of Cl nonbonding electrons. Omitting inner electrons, the configuration should be

$$(2s)^2(2s)^2(2s)^2[sa_1]^2[x_O+x_C, b_1]^2[yb_2]^2[z_O+z_{CCl_2}, a_1]^2(3p\pi)^{2\times2}(3p\pi)^{2\times2}(2p_yb_2)^2, \ ^1A_1. \qquad (7)$$
$$\text{O} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}_2\text{CO} \quad \text{O}-\text{C} \qquad \text{CCl}_2 \qquad \text{O}-\text{CCl}_2 \qquad \text{Cl} \qquad \text{Cl} \qquad \text{O}$$

The $3p\pi$'s of Cl are really each slightly split into an xb_1 and a yb_2 component, and in addition there should be resonance between the two resulting xb_1's, and between the two yb_2's. However, these splittings are doubtless not large, and will be neglected here.

In (7), it is doubtful whether the minimum I is that of $3p\pi_{Cl}$, or of $(2p_y)_O$ as in CH_2O. We know that I is 11.2 volts for $3p\pi_{Cl}$ in CH_3Cl, while I is 10.9 volts for $(2p_y)_O$ in CH_2O. It is probable that both I's are somewhat larger in $COCl_2$. Since O and Cl are competing for negative charge, the net negative charge on Cl is probably appreciably less than in CH_3Cl, and that on O less than in

H_2CO. Hence the I's should be somewhat greater.[5]

We expect that the spectrum of $COCl_2$ should contain a band system analogous to that in COH_2 near $\lambda2900$, i.e., of the type $(2p_y)_O \rightarrow [z_O-z_{CCl_2}]$ or $[x_O-x_C]$. If I is somewhat greater here for $(2p_y)_O$ than in H_2CO, and if the term value for $[z-z]$ or $[x-x]$ is nearly the same as in H_2CO, as would be expected, then these $COCl_2$ bands should be at somewhat shorter wavelengths than the corresponding bands in H_2CO. Actually the $COCl_2$ spectrum does begin at somewhat shorter

[12a] E. Eastwood and C. P. Snow, Proc. Roy. Soc. **A149**, 446 (1935).

wavelengths than that of COH_2, and resembles the latter.[13] The spectra of $(CH_3)ClCO$, (CH_2Cl)-$ClCO$, $(CCl_3)ClCO$, $(CBr_3)HCO$ are also found to be similar,[14] as might be expected; $(CCl_3)HCO$, strangely, seems to be somewhat different.

If I is nearly the same for $3p\pi_{Cl}$ as for $(2p_y)_O$ in $COCl_2$ and similar compounds, we should be inclined to expect transitions $(3p\pi_{Cl})\rightarrow X$, with absorption wavelengths near those of the transitions $(2p_y)_O\rightarrow[z-z]$ or $[x-x]$. Possibly the observed absorption near $\lambda 2500$ in these compounds,—or part of it,—is of this type.

Now suppose an S atom is substituted for the O atom in (1) or (7). There should be no formal changes in the electron configuration, only that S replaces O everywhere, and in particular, that $(3s)_S$ and $(3p_yb_2)_S$ replace $(2s)_O$ and $(2p_yb_2)_O$. An important change is that the polarities of the C—S bonding orbitals should be reduced in H_2CS and Cl_2CS, as compared with those of the corresponding C—O orbitals in H_2CO and Cl_2CO, since C and S are nearly equal in electronegativity, at least for C—S single bonds according to Pauling's scale.[4] This equality, however, may be less nearly true for C = S.

Of most interest for our purpose is I for the molecule, and its relation to the position of observed bands. The predicted I for $(3p_y)_S$ is $I^* = 10.83$ volts,[5] as compared with $I^* = 14.73$ volts for $(2p_y)_O$. The observed I for $(2p_y)_O$, as noted above, is about 10.9 volts in H_2CO, or 3.8 volts less than the predicted; this was accounted for by accumulation of negative charge on the O atom. For $(3p_y)_S$ in $\rangle C = S$ we would expect the difference between I_{obs} and I^* to be notably smaller than in corresponding $\rangle C = O$ compounds, since the net negative charge on the S must be less than on the O, possibly nearly zero.

Actually, we have no I data on compounds $\rangle C = S$, but a comparison may be made between *spectra* of these and $\rangle C = O$. In particular, data are available for Cl_2CO and Cl_2CS.[13, 15] The first

absorption region in Cl_2CO begins at about $\lambda 3042$, and reaches its intensity maximum at about $\lambda 2500$ (?). The first region in Cl_2CS begins at about $\lambda 5712$ and reaches a maximum at about $\lambda 4800$ (?); it is relatively weak. It appears fairly safe to assume that this first region of absorption in Cl_2CS is entirely analogous to that in Cl_2CO and other molecules $\rangle C = O$ and $\rangle C = S$. That is, it probably corresponds to a transition

$$(3p_y)_S\rightarrow[z_C - z_{SCl_2}] \text{ or possibly } [x_C - x_S]. \quad (8)$$

If we neglect the change in I for the *excited* orbital, which is probably not great, then the shift in frequency of the first absorption region from Cl_2CO to Cl_2CS may be taken as a rough measure of the charge in I from $(2p_y)_O$ to $(3p_y)_S$. From the rough wavelength data given above the shift is roughly about 2.4 volts, hence if I is about 11.5 volts (a reasonable estimate) for $(2p_y)_O$ in $OCCl_2$, then it is probably about $(11.5-2.4)=9.1$ volts for $(3p_y)_S$ in $SCCl_2$. This value being considerably less than the calculated $I = 10.83$ volts for $3p_S$, it appears that there must be still a considerable net negative charge on the S in $SCCl_2$, although by no means as much as on the O in $OCCl_2$.

Although the indicated considerable negative charge on the S here is rather surprising, the results are qualitatively as expected, and it appears very probable that the transition (8) in the C = S group is the cause of the color[15] possessed by many compounds of the type $S = C\langle$.

Next we may consider molecules of the types

$$O = C\langle^R_{OH} \text{ and } O = C\langle^R_{OR'}, \text{ also } O = C\langle^{OR}_{OR'}$$
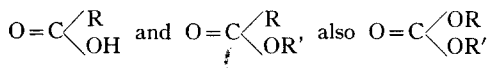
(organic acids and esters). In such cases one might expect to find absorption band systems corresponding to the electron transitions within the C = O group, exactly like those in the aldehydes and ketones, except that in the acids RCOOH, there is a modifying influence in the

[13] V. Henri, *Structure des Molecules* (Paris, 1925). Cf. especially pp. 88–92, and the plates.

[14] R. A. Rehman, R. Samuel and Sarf-ud-Din, Ind. J. Phys. 8, 537 (1934).

[15] Purvis, Jones and Tasker, J. Chem. Soc. (London) 110, 520 (1924). Absorption spectra of $SCCl_2$, $SC(OR)_2$, $SC(OR)(SR)$, $SC(SR)_2$, $OC(OR)_2$, $OC(OR)(SR)$, $OC(SR)_2$

etc. in dilute ethyl alcohol solutions. $SCCl_2$ is reported to be an orange-red liquid. In all these cases, the absorption is reported to begin in the ultraviolet. Apparently the solutions were too dilute for the detection of the comparatively weak visible absorption system of the $\rangle C = S$ types, found[13] by Henri in $CSCl_2$, and whose presence must be responsible for the colors reported for some of these substances.

fact that the H atom may be labile and tend to jump from one O atom to the other, or to locate itself between them. These expectations seem to be confirmed by the experimental evidence, but a detailed consideration will not be undertaken here.

S.milarly, molecules like

$$S=C\diagdown{\genfrac{}{}{0pt}{}{R}{OR}}, \quad S=C\diagup{\genfrac{}{}{0pt}{}{OR}{OR'}}$$
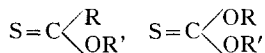
etc., should have characteristic S=C absorption[15] like that in S=CCl₂. The same is true of molecules like

$$S=C\diagup{\genfrac{}{}{0pt}{}{OR}{SR}}, \quad S=C\diagup{\genfrac{}{}{0pt}{}{SR}{SR''}}, \quad S=C\diagup{\genfrac{}{}{0pt}{}{R}{SR}}$$
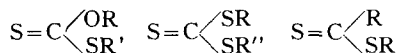
etc.[15] In all these cases, the molecule must *also* be regarded as a derivative of H_2O or H_2S, and there should be absorption regions, but at shorter wavelengths than the first absorption region of the C=O or C=S, associated with excitation of np nonbonding electrons of the single-bonded O or S atoms.[1] It is interesting to note that, although the most easily excited electron in both $\diagup$C=O and $\diagup$O is found to be a nonbonding $2p$ electron of the O atom, excitation is easier in the former case, partly because I is lower there for the nonbonding electron, and partly because I is higher for the lowest available excited orbital there. Analogous statements hold, of course, for the S compounds.

Electronic Structures of Molecules

XI. Electroaffinity, Molecular Orbitals and Dipole Moments

ROBERT S. MULLIKEN, *Ryerson Physical Laboratory, University of Chicago*
(Received June 25, 1935)

A convenient criterion for defining equal electronegativity of two atoms is stated in terms of coefficients in LCAO approximate molecular orbitals. Connections between relative electronegativities, coefficients in LCAO orbitals, effective charges on atoms in partially polar molecules, and dipole moments, are then analyzed, and various equations are obtained expressing these connections. The discussion is largely applicable to polyatomic as well as to diatomic molecules. A theoretical derivation is given for an empirical equation, found by Pauling, which forms a basis for the latter's approximate scale of relative electronegativities. Pauling's and other possible approximate scales are discussed, and it is shown how an approximate "absolute electroaffinity" can conveniently be defined on each scale. A very rough theoretical justification is given for the empirically observed proportionality between relative electronegativities obtained from Pauling's and from the writer's scale. The necessary existence of a "homopolar dipole" contribution to the electric moment of any bond is shown, provided the atoms forming the bond are of unequal size. By "homopolar dipole" is meant a contribution which would not vanish, for atoms of unequal size, even if they are of equal electroaffinity. Dipole moments of H_2O, NH_3 and HX are briefly discussed. It is concluded that the dipole moment scale of electronegativity is probably not well founded. An important object of the paper is to show how electroaffinity and other data can be used in the approximate determination of the polarities of molecular orbitals and so of bonds, the results being expressed both in terms of coefficients in LCAO molecular orbitals and in terms of effective charges transferred. Applications are made to the electronic structures of various diatomic molecules, especially HI, HI^+, HO^-, ClO^-.

1. INTRODUCTION

IN determining the electron configurations of molecules, we may proceed semi-empirically by considering alternative possibilities based on rough theoretical schemes, and then making choices in harmony with empirical data. The most convenient simple and generally applicable way of working out such theoretical schemes with molecular orbitals is to use LCAO approximations for the latter, at least for the normal and some of the low excited states. By using these in connection with certain semi-empirical rules it is possible even to make approximate predictions of I's (ionization potentials) for the real (Hartree-