Electronic Structures of Polyatomic Molecules. IX. Methane, Ethane, Ethylene, Acetylene

Robert S. Mulliken

Additional information on J. Chem. Phys.

Summarizing, we conclude that the deviations $I_{pred} - I_{obs}$ for nonbonding atomic orbitals are mainly due to charge-transfer (except in HX?), and that the use of such localized nonbonding atomic orbitals gives good approximations; also that intraradical-bonding orbitals such as $[\pi e]$ of CH_3 may safely be considered as localized, i.e., treated as radical orbitals which are nonbonding so far as interactions with other orbitals are concerned. This last conclusion is in harmony with other evidence in regard to relations between parent molecules and their derivatives.[4]

II. Bonding and Antibonding Orbitals

It is obvious that charge-transfer effects should be important not only for the I's of nonbonding orbitals, but also for those of bonding and antibonding orbitals. Price[7] has already emphasized the importance of dipole effects in this connection. The semi-empirical rules previously set up[5] may be stated as follows:

$$I_{pred} \gtrless \tfrac{1}{2}(I_A{}^\circ + I_B{}^\circ), \qquad (1)$$

where the upper inequality sign refers to bonding, the lower to antibonding orbitals, and the I°'s are calculated as earlier indicated.[5] A and B refer to the two atoms forming the bond; if the orbital is a nonlocalized one involving several atoms, the necessary generalization of (1) is easily made. If atoms A and B have effective net charges, the I°'s and I_{pred} must be altered accordingly, but probably not more than 1 or 2 volts in most cases for neutral molecules. Just how large such corrections should be may perhaps best be determined by experience. The same applies to the magnitude of the inequalities indicated by (1); in practice these appear usually to be of the order of 1–3 volts.

For a heteropolar bond involving the usual electron-pair (i.e., excluding the case of one-electron bonds), the charge-transfer effect will generally tend to make $I_A{}^\circ$ and $I_B{}^\circ$ more nearly equal than they are for the free atoms. This is because the more electronegative atom usually has the larger I°, which should then usually be decreased by charge-transfer, while the smaller I°, belonging to the more electropositive atom, is at the same time increased. For a homopolar bond, $I_A{}^\circ$ and $I_B{}^\circ$ will both be increased or decreased together by charge-transfer, if any. Here the transfer is to or from A and B, from or to other atoms in the molecule. (Example: $C-C$ bonding orbital in C_2H_6, where I°'s should be decreased due to $H_3{}^+C^-$ polarities. This may be expressed, following Price,[7] by saying that I should be decreased by the effects of the two $C^-H_3{}^+$ dipoles.)

In XI of this series it will be shown that the use of molecular orbitals logically implies a comparison not with I°'s of atoms which (at least for the average of A and B) are neutral, but with much smaller I°'s, call them N°'s, corresponding to a condition (cf. Hund) about half-way between neutral atom and negative ion. Instead of (1), this would yield the condition $I_{pred} \gg \tfrac{1}{2}(N_A{}^\circ + N_B{}^\circ)$ for bonding and perhaps $I_{pred} > \tfrac{1}{2}(N_A{}^\circ + N_B{}^\circ)$ for antibonding orbitals. Such relations, however, are probably unfruitful, since the N's are not accurately known and the magnitudes of the inequalities are large. In practice, the as yet essentially empirical relations (1) promise to be much more useful, since experience so far has shown them reliable.

Electronic Structures of Polyatomic Molecules. IX. Methane, Ethane, Ethylene, Acetylene

Robert S. Mulliken, *Ryerson Physical Laboratory, University of Chicago*
(Received May 21, 1935)

Electron configurations for the normal states of C_2H_6, C_2H_4, and C_2H_2 are given, and are used in interpreting observed ionization potentials. Excited orbitals of CH_4 and the others are also discussed and tentative interpretations given for the ultraviolet spectra. "Reduced" interatomic distances are studied as a measure of overlapping and resonance of orbitals of different atoms or radicals.

I. Methane

THE CH_4 problem has already been considered in previous papers[1] but some additional points, especially in regard to excited states, will be taken up here, mainly for the sake of comparisons with ethane and other molecules. The normal and probable lowest excited states of CH_4 (symmetry T_d) are

$$1s^2[sa_1]^2[pt_2]^6, {}^1A_1 \text{ and } [pt_2]^{-1}(3sa_1), {}^{1,3}T_2$$
$$I_{vert} = \quad 22_{est} \quad 14.4_{obs}. \qquad (1)$$

The symbol $[p]^{-1}(3s)$ means that one $[p]$ electron has been abstracted from the *normal* configuration, and one $(3s)$ has been added; i.e., it means $1s^2[sa_1]^2[pt_2]^5(3sa_1)$.

It is of interest first to compare the observed I (14.4 volts) with that predicted by the usual rules.[2] According to these, we expect

$$I([pt_2]) > \tfrac{1}{2}\{I^\circ(1s_H) + I^\circ(2p_C)\}. \qquad (2)$$

By methods given previously,[3] $I^\circ(2p_C) = 11.21$ volts, while $I^\circ(1s_H) = 13.53$ volts, so that we predict $I([pt_2]) > 12.37$. Thus the inequality sign here corresponds to about 2 volts, a reasonable value (cf. the case of H_2, where with a bond of comparable or somewhat greater strength, the inequality amounts to 2.4 volts). Proceeding in a similar manner, we may estimate I for $[s]$ of CH_4 as roughly about 22 volts, as given under (1). No experimental value to check this is available.

As lowest excited orbitals of CH_4, it seems reasonable to expect Rydberg, i.e., large atom-like, orbitals $3s$, $3p$, $3d$, etc., with $3s$ lowest. In previous papers,[1] certain LCAO approximate forms[4] were given for CH_4 orbitals, namely, $C-H$ bonding forms corresponding to $[sa_1]$ and $[pt_2]$ of (1), and certain complementary forms called $[s^*a_1]$ and $[p^*t_2]$, similar to $[s]$ and $[p]$, respectively, but of consistently $C-H$ antibonding instead of $C-H$ bonding character. Examination of the nodal surfaces of the LCAO forms $[s^*]$ and $[p^*]$ shows that they are qualitatively very similar to those of $3s$ and $3p$ of an atom. It seems

altogether probable, therefore, that $[s^*]$ and $[p^*]$ should be identified with Rydberg orbitals $3s$ and $3p$; and also probable that in this case the *real* molecular orbitals can be much better approximated by suitable $3s$ and $3p$ atomic orbitals, i.e., penetrating central-field orbitals, than by LCAO forms.

An analogous case is that of $(1s-1s, \sigma_u)$,—in LCAO symbolism,—of H_2, which in its form, for small r, closely resembles $2p\sigma_u$ of an atom, and does in fact go over into $2p\sigma_u$ of the united-atom as $r \to 0$, and is in fact legitimately considered as $2p\sigma_u$ in the listing of the He-atom-like Rydberg-series-forming excited orbitals of the H_2 molecule.[5]

The selection rules of symmetry T_d allow transitions from the normal state ${}^1A_1$ to the excited state ${}^1T_2$ of (1), also very much weaker transitions to the ${}^3T_2$. The transition ${}^1A_1 \to {}^1T_2$ should be strong, since the one-electron jump $[pt_2] \to 3sa_1$ involved is similar to $2p \to 3s$ of an atom: in form $[pt_2]$ strongly resembles $2p$ of an atom.[1] We may then reasonably identify the first intensity maximum (λ about 1250) of the continuous CH_4 absorption[6] with the vertical excitation energy of the transition ${}^1A_1 \to {}^1T_2$ ($[p] \to 3s$); we thus get 9.9 volts for that energy. Subtracting this from the observed I (electron-impact, adiabatic?), we get 4.5 volts for the term value of $3s$ in ${}^1T_2$, a reasonable value. This result may be compared with the values 4.6 and 5.2 volts obtained in a similar way for $3s$ from the ultraviolet spectra of NH_3 and H_2O, respectively.[7] (Cf. also the term values 3.85 and 4.20 volts for $3s$ of the N atom in the ${}^2P$ and ${}^4P$ states of $[N^+({}^3P) \cdot 3s]$ and the values 4.08 and 4.45 volts for $3s$ of the O atom in the ${}^3S$ and ${}^5S$ states of $[O^+({}^4S) \cdot 3s]$.) The continuous or diffuse character of the spectra in CH_4, as in NH_3 and H_2O, is attributed to strong predissociation.

The foregoing might lead one to wonder whether in general all excited orbitals of molecules are atom-like Rydberg orbitals. Many well-known examples in diatomic molecules show definitely, however, that this is not the case.

[1] R. S. Mulliken, J. Chem. Phys. **1**, 490 (1933): V of this series; see p. 500 for CH_3. Also XII of this series, J. Chem. Phys. 1935, in connection with forms and polarities of orbitals.

[2] R. S. Mulliken, J. Chem. Phys. 514: VIII of this series.

[3] a. R. S. Mulliken, Phys. Rev. **46**, 551 (1934); b. J. Chem. Phys. **2**, 789 (1934).

[4] R. S. Mulliken, J. Chem. Phys. **3**, 375 (1935): VI of this series.

[5] Cf. R. S. Mulliken, Rev. Mod. Phys. **4**, 1 (1932).

[6] A. B. F. Duncan and J. P. Howe, J. Chem. Phys. **2**, 851 (1934).

[7] R. S. Mulliken, J. Chem. Phys. **3**, 506 (1935): VII of this series.

For comparison of CH_4 with certain derivatives, Eq. (1) may be replaced by formulations assuming the symmetry reduced to C_{3v} by a slight distortion. We have

$$[sa_1]^2[\pi e]^4[\sigma a_1]^2, \; {}^1A_1; \; [\sigma a_1]^{-1}(3sa_1) \; {}^{1,\,3}A_1 \text{ and}$$
$$[\pi e]^{-1}(3sa_1), \; {}^{1,\,3}E. \quad (3)$$

The orbital $[pt_2]$ of (1) splits into $[\pi e]$ and $[\sigma a_1]$ and the excited states ${}^{1,\,3}T$ split into ${}^{1,\,3}A_1$ and ${}^{1,\,3}E$.

II. ETHANE

In connection with the following discussion of C_2H_6, C_2H_4 and C_2H_2, it is of some importance to know how the distance r_e between the two C nuclei compares with the sizes of $2s$ and $2p$ orbitals of carbon. The results can best be expressed in terms of the quantity[5] $\xi = r_e/2r_a$, where r_a is an effective radius of the $2s$ or $2p$ orbital. Slater gives empirical rules for evaluating r_a roughly; these assume the same r_a for $2s$ and $2p$.[7a] Table I gives values of r_e and ξ for C_2H_n and for some diatomic molecules with which it is of interest to compare these. The r_e data in Table I, except for C_2H_6 and C_2H_4 (electron diffraction) and F_2 (uncertain estimate), are from band spectra.[7b] Although the r_a values have only a rough meaning, they suffice to show that the two C atoms in each C_2H_n are always more compressed, in terms of ξ, than are the two atoms in the isoelectronic diatomic molecule.

The electron configuration of ethane can perhaps best be approximated by treating it, as nearly as may be, as a derivative of CH_4, just as N_2H_4 and H_2O_2 were treated as derivatives of NH_3 and H_2O in a previous paper.[7] Other derivatives of CH_4, in particular those of the type CH_3X, have been discussed in another paper,[8] to which reference should be made. It is also instructive to compare C_2H_6 with the isoelectronic molecule F_2.

The symmetry of C_2H_6 is either D_{3h} (trigonal prism), D_3, or D_{3d} according to the relative angular orientation of the two CH_3 groups around their common axis of symmetry. Although the energy is a minimum for D_{3d} and a maximum for

TABLE I. *Molecular dimensions.*

No. Elecs.	Molecules	r_e(A.)	ξ	Molecule	r_e	ξ
18	C_2H_6	1.55	1.2	F_2	1.4?	1.7?
16	C_2H_4	1.32	1.0	O_2	1.20	1.3
14	C_2H_2	1.20	0.9	N_2	1.09	1.0
				Cl_2	1.98	1.3

D_{3h}, the difference is probably so small[8a] that essentially "free rotation" occurs, and the symmetry D_3 characteristic of intermediate rotation angles may be taken as typical. Consideration of D_{3h} and D_{3d} is principally of interest in connection with electronic selection rules, since some transitions which are allowable according to the relatively liberal selection rules of D_3 are forbidden according to those of D_{3h} or of D_{3d} or sometimes of both.* In such cases we are justified in concluding that the transitions in question are weak even for D_3.

If we assume symmetry D_3, the normal state of C_2H_6, omitting carbon $1s$ electrons, may be described as

$$[sa_1]^2[sa_1]^2[\pi e]^4[\pi e]^4[\sigma+\sigma, a_1]^2, \; {}^1A_1$$

approx. (4)

location CH_3 CH_3 CH_3 CH_3 H_3C-CH_3

est. vert. I two values   two val.

aver. about   close to

22?   14.5   12

All the orbitals used in (4) are CH_3 radical orbitals, except for the $C-C$ bonding orbital $[\sigma+\sigma]$, which may be thought of as built approximately from $[\sigma]$'s of two CH_3 radicals. The electron configuration (4) has a strong similarity to that of a halogen molecule, in particular F_2, for which we have[3a]

$$(2s)^2(2s)^2(2p\pi)^4(2p\pi)^4(2p\sigma+2p\sigma, \; \sigma_g)^2, \; {}^1\Sigma_g{}^+.$$
$$\text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad\quad \text{F}-\text{F}$$

Resonance between the two $[\pi e]$'s in (4) should of course exist, but is probably weak (see below) and should then give rise to only a small splitting of the I value. It can then be predicted that the latter should not differ much from the value 14.4 volts for $[\pi e]$ in CH_4 (cf. (1), (3) above), since the field of force for $[\pi e]$ here should not be much different than in CH_4 or CH_3X.[8]

[7a] Cf. J. C. Slater and N. H. Frank, *Introduction to Theoretical Physics* (McGraw-Hill & Co., 1933), p. 432.
[7b] Cf. R. de L. Kronig, *The Optical Basis of Chemical Valence* (MacMillan Co., New York, 1935).
[8] R. S. Mulliken, Phys. Rev. **47**, 413 (1935).

[8a] Cf. H. Eyring, J. Am. Chem. Soc. **54**, 3200 (1932). K. Yardley, Proc. Roy. Soc. **A118**, 449 (1928) finds symmetry D_{3d} for C_2Cl_6 (in crystals).
* Cf. reference 11.

The strength of resonance between pairs of orbitals like the foregoing $[\pi e]$ or the two $[sa_1]$ in (4) can be gauged somewhat by the ξ values in Table I, as compared to what is known for molecules like N_2 and O_2. We know that in N_2, resonance between π orbitals of the two atoms is strong, giving $(\pi+\pi)$ and $(\pi-\pi)$. The same is true in O_2, but probably not in F_2 or other halogens.[2] Although ξ for C_2H_6 is less than for O_2, this is not a fair indication of the degree of overlapping of the $[\pi e]$'s of the two CH_3. Since the $[\pi e]$'s give strong $C-H$ bonding in each radical, they are doubtless concentrated largely between the H_3 plane and a parallel plane through the carbon nucleus, but with centers of gravity somewhat nearer the H_3 plane; in size and form they perhaps resemble $2p\pi$ orbitals of an N or O atom (cf. discussion of $[p\pi]$ orbitals of $\cdot CH_4$ in V of this series, section 11 and Eqs. (6); also in XII of this series). The height of the CH_3 pyramid, assuming tetrahedral valence angles, is $\frac{1}{3}$ of the $C-H$ distance, i.e., about $\frac{1}{3}$ of 1.1A, or 0.36A. Thus the center of gravity of each $[\pi e]$ is about 0.2A from the C atom, so that the mean distance apart of $[\pi e]$ orbitals of the two CH_3 radicals is about 0.4A greater than the $C-C$ distance, or about 1.95A. This gives for them an effective ξ of 1.5 if we use r_a of the C atom, or somewhat more if a more suitable effective ξ is used. Thus the degree of overlapping of the $[\pi e]$'s in C_2H_6 is clearly much smaller than that of the π's in O_2, probably comparable with that of the π's in F_2, so that resonance between them should be small. This justifies our use of radical orbitals $[\pi]$ rather than whole-molecule orbitals $[\pi+\pi]$ and $[\pi-\pi]$.

In the case of N_2 we know, from the value of an I which must be attributed to $(s-s)$, that there is very strong resonance between the atomic $2s$ orbitals, so that the use of $(s+s)^2(s-s)^2$ gives a better approximation[3a] than the use of $2s^2 2s^2$. For $2s$ of O, there is no direct evidence from band spectra or I's, yet it is hard to believe that there is not strong resonance between the $2s$'s in view of the existence of strong resonance for the $2p\pi$'s, for which the overlapping is less favorable than for the $2s$'s. (It should be noted that, for a given ξ, strong overlapping sets in at smaller r values for $p\pi$'s than for $p\sigma$'s or s's. Really, it would be more logical to give a separate ξ for the π orbitals, using the same r_e but smaller r_a.)

Resonance between the $[sa_1]$ orbitals of the two CH_3 in C_2H_6 is probably fairly strong (unlike the case of F_2), since ξ has a value between those of N_2 and O_2 and since in CH_4 the orbital $[sa_1]$ is not restricted to a CH_3 group but also helps hold the fourth H, which is here replaced by a second CH_3 group. For strong resonance one should write

$$[s+s, a_1]^2[s-s, a_2]^2[\pi e]^4[\pi e]^4$$
$$[\sigma+\sigma, a_1]^2, \ ^1A_1. \quad (4a)$$

Here I should be considerably greater for $[s+s]$ than for $[s-s]$. The orbitals $[s \pm s]$ in LCAO approximation are constructed as linear combinations of $[s]$ orbitals of the two CH_3 and so, like the latter, involve considerable $C-H$ bonding.

At the same time, one has to admit some interaction between $[s+s]$ and $[\sigma+\sigma]$, giving two new partially mixed forms; such hybridization should increase I for $[s+s]$ and decrease it for $[\sigma+\sigma]$. It is difficult to estimate the extent of this mixing effect, but the writer is inclined on the whole to think that it is not large.

The $C-C$ bonding orbital $[\sigma+\sigma]$ must be admitted to give a little bonding between each C and its 3H, as one sees by comparison with the related orbital $[\sigma a_1]$ of CH_4. Hence $[\sigma+\sigma]$ is not quite completely localized in the $C-C$ bond. If, however, we neglect this and also neglect mixing with $[s+s]$, $[\sigma+\sigma]$ may be represented roughly by

$$a(2p\sigma+2p\sigma),$$

and has approximately the symmetry σ_g of the bonding orbital $(\sigma+\sigma)$ of a diatomic molecule like F_2. Following the usual rule,[2] we may predict that

$$I_{vert}(\sigma+\sigma) > I^{\circ}(2p\sigma_C).$$

By methods given previously,[3] one obtains $I^{\circ}=11.21$ volts for $2p\sigma_C$, hence one predicts $I(\sigma+\sigma) > 11.21$ volts. Since the $C-C$ bond in C_2H_6 is strong, one might expect the inequality sign to represent perhaps about 2 volts as in typical cases with strong bonds. In accordance with a point made by Price,[9] to the effect that I of the $C-C$ bonding electron must be reduced by the fields of the two CH_3 dipoles (polarity $H_3^+C^-$), it seems likely that above-estimated I° should be reduced by as much as 1 or 2 volts. The

[9] W. C. Price, Phys. Rev. 47, 444 (1935): C_2H_2, C_2H, C_2H_6.

net result is a predicted value of about 11 or 12 volts for the vertical I of $(\sigma+\sigma)$. The adiabatic I should be considerably less, since the $C-C$ bonding should be markedly loosened by removal of one of the two $[\sigma+\sigma]$ electrons.

Another mode of approach is to consider the formation of C_2H_6 from two CH_3. The structure of CH_3 is given by

$$[sa_1]^2[\pi e]^4[\sigma a_1], \ ^2A_1,$$

and I_{vert} for $[\sigma a_1]$ is believed to be about 8.5 or 9 volts, both for free CH_3 (which may be plane) and for CH_3 constrained to the shape it has within C_2H_6.[1] Now $[\sigma+\sigma, a_1]$ of C_2H_6 and $[\sigma a_1]$ of CH_3 are related in the same way as, e.g., $(\sigma+\sigma, \sigma_g)$ of F_2 and $2p\sigma$ of F. Hence we might expect

$$I_{vert}([\sigma+\sigma]) > I^\circ_{vert}([\sigma a_1]).$$

Here I°_{vert} is just I_{vert} of $[\sigma a_1]$ of CH_3. If we assume 2.5–3 volts for the inequality sign, I_{vert} $([\sigma+\sigma])$ comes out again with a predicted value of 11–12 volts.

Experimentally, we have only Morris' electron-impact value[10] of 12.8 volts for I of C_2H_6. Since Morris' values for C_2H_4 and C_2H_2 were, respectively, 12.2 and 12.3 volts, as compared with the values 10.41 and 11.35 determined later by spectroscopic methods,[9] we may apply a correction of about -1.4 volts to Morris' value, giving as a probable corrected experimental value 11.4 volts. This, however, would be an adiabatic value, and the true vertical value might then be about 12.4 volts, which is in reasonable agreement with our estimates. At any rate, there seems to be little doubt that the minimum I of C_2H_6, whether measured vertically or adiabatically, must belong to $[\sigma+\sigma]$.

Turning now to excited orbitals and states of C_2H_6, it appears likely that the lowest excited orbital is of essentially $3s$ type. In analogy to our previous discussions[7] of N_2H_4 and H_2O_2, we might first think of a $3s$ orbital for each CH_3 radical. Since these overlap strongly, however, we should then form linear combinations $a(3s\pm3s)$, of which the form $a(3s+3s)$ must have the lower energy. It is readily seen that this form is rather closely similar to that of a single $3s$ function centered about the mid-point of the $C-C$ line. The lowest excited states may well be those ob-

tained by exciting one $[\sigma+\sigma, a_1]$ electron of (4) and putting it into $3sa_1$, giving

$$[\sigma+\sigma, a_1]^{-1}(3sa_1), \ ^{3, \ 1}A_1. \tag{5}$$

On examining the electronic selection rules for symmetry D_3, however, we find that transitions from A_1 to A_1 are forbidden,[11] so that $(4)\rightarrow(5)$ should not occur. [Weak violations of this prohibition may nevertheless occur because of coupling between electronic and vibrational motions.[11a]]

What, then, are the lowest excited states to which transitions are not forbidden? If one of the $[\pi e]$ electrons of (4) is excited to $3sa_1$, the result is

$$[\pi e]^{-1}(3sa_1), \ ^{1, \ 3}E, \ ^{1, \ 3}E. \tag{6}$$

Transitions from $^1A_1$ to ^1E (and weakly to ^3E) are allowed, and one of these should in fact probably be strong, the electron transition being essentially $[\pi e]\rightarrow3s$ within either CH_3 radical, resembling $2p(\pi)\rightarrow3s$ of an atom.

There are two ^1E and two ^3E in (6) because of resonance between the configurations $[\pi]^4[\pi]^3$ and $[\pi]^3[\pi]^4$ which are implied by $[\pi]^{-1}$. This resonance corresponds to an incipient tendency toward two conditions which we could express in LCAO symbols[4] by writing $[\pi+\pi, e]^4[\pi-\pi, e]^3$ and $[\pi+\pi, e]^3[\pi-\pi, e]^4$. Recognizing that $3sa_1$ here is of the LCAO type $(3s+3s, a_1)$, one finds that the only strong transition is the $^1A\rightarrow^1E$ involving the ^1E state of type $[\pi+\pi]^3[\pi-\pi]^4$, the higher-energy one of the two. This follows if we note that for symmetry D_{3d}, state (4) is $^1A_{1g}$ while (6) becomes $^{1, \ 3}E_g$ (lower), $^{1, \ 3}E_u$ (higher), the latter involving $[\pi+\pi, e_u]^3[\pi-\pi, e_g]^4(3s+3s, a_{1g})$; only $g\rightarrow u$ transitions are allowed for symmetry D_{3d}.

We are now in a position to understand the observed close similarity[10, 12] of general appearance between the ultraviolet spectra of CH_4 and C_2H_6. In both cases the spectrum is continuous with indications of only a few diffuse bands. Very faint absorption begins near $\lambda1800$, at least in CH_4 (1 atmos. pressure, 15 mm path). The intensity increases steadily as λ decreases, reaching a maximum in CH_4 near $\lambda1250$, and in C_2H_6 near $\lambda1350$, so far as can be judged by the published descriptions.[6, 9] This close similarity is just what we should expect assuming that in both cases we have an excitation process $[\pi e]\rightarrow3s$, with nearly the same energy relations in both

[10] J. C. Morris, Phys. Rev. **32**, 456 (1928).

[11] R. S. Mulliken, Phys. Rev. **43**, 279 (1933).
[11a] Cf. G. Herzberg and E. Teller, Zeits. f. physik. Chemie **B21**, 410 (1933).
[12] G. Scheibe and H. Grieneisen, Zeits. f. physik. Chemie **B25**, 52 (1934).

cases. As we have seen, I is expected to be about the same for $[\pi e]$ in C_2H_6 as in CH_4, while the term value of $3s$ may well also be nearly the same in both.

Of course in CH_4, $[\pi e] \rightarrow 3s$ is accompanied by and coincident with $[\sigma a_1] \rightarrow 3s$, since $[\pi e]$ and $[\sigma a_1]$ of symmetry C_{3v} together make $[pt_2]$ for symmetry T_d (cf. (1) and (3)). In C_2H_6, however, the transition $[\sigma+\sigma] \rightarrow 3s$, although it rather corresponds to $[\sigma a_1] \rightarrow 3s$ of CH_4, would come at much longer wavelengths (absorption maximum perhaps near $\lambda1600$),—see above. If this transition were not forbidden in C_2H_6, the similarity in wavelength distribution between the CH_4 and C_2H_6 spectra would not occur.

Before the matter of C_2H_6 excited states is dismissed, the $C-C$ antibonding excited orbital $[\sigma-\sigma, a_2]$ should be mentioned (cf. discussion of analogous orbitals in H_2O_2 and N_2H_4).[7] Examination of the form of this shows that its nodal surfaces resemble those of the atomic orbital $3p\sigma$ and it seems likely that $[\sigma-\sigma]$ plays this role in C_2H_6.
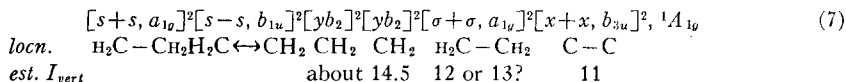
Cf. the $C-H$ antibonding orbitals $[s^*]$ and $[p^*]$ in CH_4 (obtained by LCAO methods), which apparently function as, or are replaced by, $3s$ and $3p$. In C_2H_6, as we have seen, our $3s(C_2H_6)$ corresponds to an LCAO form $[3s(CH_3)+3s(CH_3)]$, while $3s(CH_3)$ in turn corresponds to an LCAO $C-H$ antibonding form $[s^*]$ similar to that of CH_4. Similarly $3p\pi(C_2H_6)$ may be identified with the LCAO form

$$[3p\pi(CH_3)+3p\pi(CH_3)] \approx \{[\pi^*](CH_3)+[\pi^*](CH_3)\}.$$

The writer is inclined to think that the excited states derivable by exciting a $[\sigma+\sigma]$ electron to $[\sigma-\sigma]$ are higher than those of either (5) or (6), or at least than those of (5). Reasons for this opinion will be given in a later paper dealing more systematically with excited orbitals.

III. Ethylene

Ethylene has already been discussed in previous papers.[11, 13, 12a] In its normal state (symmetry V_h), the electron configuration, omitting carbon $1s$, can perhaps best be represented by

$$[s+s, a_{1g}]^2[s-s, b_{1u}]^2[yb_2]^2[yb_2]^2[\sigma+\sigma, a_{1g}]^2[x+x, b_{3u}]^2, \, {}^1A_{1g} \qquad (7)$$

locn. $\quad H_2C-CH_2 \, H_2C \leftrightarrow CH_2 \, CH_2 \quad CH_2 \quad H_2C-CH_2 \quad C-C$

est. I_{vert} $\qquad\qquad\qquad$ about 14.5 $\quad$ 12 or 13? $\qquad$ 11

Here $[\sigma+\sigma]$ might just as well be called $[z+z]$, but we shall use $[\sigma+\sigma]$ because it is used for a corresponding orbital in C_2H_6, C_2H_2 and other cases. The axes z, y, x are, respectively, along the $C-C$ axis, in the plane of the molecule perpendicular to this axis, and perpendicular to the plane of the molecule. The representation symbol b_2 belonging to the CH_2 radical orbitals in (7), belongs to the local symmetry (C_{2v}) of these radicals. The other representation symbols a_{1g}, b_{1u}, b_{3u} in (7) belong to the symmetry V_h of the molecule-as-a-whole.

Attention should perhaps be called to the meaning and implications of the orbital symbols in (7). The symbol $[s+s]$ means a certain whole-molecule orbital which could be *approximately* built by taking $a\{[s]_A+[s]_B\}$, where $[s]$ refers to an orbital of one of the CH_2 radicals. The symbol $[s]$ in turn represents an orbital which could be built in LCAO *approximation* from a linear combination of $2s$ of carbon and $1s$ of two H atoms (cf. IV of this series). Since $[s]$ involves $C-H$ bonding, so does $[s+s]$, but $[s+s]$ also involves $C-C$ bonding. The estimated relative

importance of $C-H$ and $C-C$ bonding for the various orbitals is indicated under the electron configuration in (7). It will be noted that $[s+s]$, $[s-s]$, and $[\sigma+\sigma]$ are inter-radical orbitals of completely nonlocalized type.

The orbitals $[y]$ are localized to the extent of being each restricted to one CH_2 radical, although not localized within the latter. The symbol $[x+x]$ describes an orbital which can be constructed in LCAO approximation as $a\{(2p_x)_A +(2p_x)_B\}$, where each $2p_x$ is a CH_2 radical orbital which happens to be of particularly simple type, being, namely, just a nonbonding C atom orbital. Because each $2p_x$ is localized on the C atom of CH_2, $[x+x]$ is partially localized in C_2H_4, being confined to the $C-C$ bond. It is an inter-radical orbital, but of semi-localized type.

[12a] C. P. Snow and Alsopp, Trans. Faraday Soc. **20**, 93 (1934) have recently made a careful study of the ultraviolet spectra of C_2H_4 and some of its derivatives. This supports (9) as upper level of the C_2H_4 bands. This paper was unfortunately overlooked until the present paper was in proof.

[13] a. R. S. Mulliken, Phys. Rev. **41**, 751 (1932). b. Also W. G. Penney, Proc. Roy. Soc. **A144**, 166 (1934); Proc. Phys. Soc. London **46**, 333 (1934): C_2H_4 and C_2H_6.

The electron configuration (7) of C_2H_4 has relations[13a] to that of the isoelectronic molecule O_2, but they are much less close than those between the configurations of C_2H_6 and F_2, or of C_2H_2 and N_2. This is because the change of symmetry from C_2H_4 to O_2 is much more radical than from C_2H_6 to F_2, or C_2H_2 to N_2 (no change at all in the latter).

If (7) is used for C_2H_4, we must admit the existence of resonance and a double I for the two $[y]$ orbitals. This resonance must be stronger than that of the two $[\pi]$'s in C_2H_6 or the two π's in F_2, but is probably still not very strong. An effective ξ can be estimated in the same way here for the $[y]$'s of the two CH_2 as was done above for the $[\pi]$'s of the two CH_3 in C_2H_6. Assuming an $H-C-H$ angle of 120°, the center of gravity of each $[y]$ orbital is about 0.3A from the C atom, and the mean distance between the two $[y]$'s is about 1.9A. This makes the effective ξ nearly as great as for the $[\pi]$'s in C_2H_6, and much greater than for the $2p_z$'s which are used to form $[x+x]$ here, since the latter involve no $C-H$ bonding and are centered at the carbon atoms.

There must be more or less mixing between the pure LCAO forms $[s+s, a_{1g}]$ and $[\sigma+\sigma, a_{1g}]$ and again between $[s-s, b_{1u}]$ and $[\sigma-\sigma, b_{1u}]$, the last an excited type not present in (7). The mixing is probably stronger than for the analogous C_2H_6 orbitals, in view of the smaller ξ (cf. Table I) and the stronger $C-C$ bond. It is difficult to devise a simple yet descriptive LCAO symbolism to indicate such mixing. If we had complete, i.e., 50–50, mixing, it would be best to replace the symbols $[s\pm s]$ and $[\sigma\pm\sigma]$ by new symbols such as $[q^+\pm q^+]$ and $[q^-\pm q^-]$. If for the moment we neglect the participation of hydrogen $1s$ functions in $[s]$ and $[\sigma]$, then the q's represent 50–50 mixtures of carbon $2s$ and $2p\sigma$, of the same sort that occur in the linear Stark effect of the H atom for $n=2$. (These q's have been used by Pauling under the designations σ_b, σ_0 in discussing the structure of N_2.) We should then have

$$q^+ = 2^{-\frac{1}{2}}(2s+2p\sigma), \quad q^- = 2^{-\frac{1}{2}}(2s-2p\sigma),$$

where the signs are to be so understood that each q^+ is strong in the direction of the other C atom, q^- in the direction of the neighboring H atoms. Instead of the q's just given, corresponding $[q]$'s

in which hydrogen $1s$ functions participate must of course be used in constructing the forms $[q\pm q]$ which we are considering.

For the ideal case of 50–50 $s-p\sigma$ mixing, (7) would be replaced by

$$[q^++q^+, a_{1g}]^2[q^--q^-, b_{1u}]^2[q^-+q^-, a_{1g}]^2$$
$$\times [yb_2]^2[yb_2]^2[x+x, b_{3u}]^2, \, {}^1A_{1g}. \quad (7a)$$

The actual case must be intermediate between (7a) and that which is represented by (7) if in the latter the symbols $[s\pm s]$ and $[\sigma+\sigma]$ are taken to represent pure LCAO forms without any $s-p\sigma$ mixing. For the sake of simplicity, however, we shall in practice *let the symbolism in (7) represent the intermediate case* just described. That is, we shall in practise use $[s+s]$ to represent something between the pure $[s+s]$ and $[q^++q^+]$, $[s-s]$ something between pure $[s-s]$ and $[q^--q^-]$, $[\sigma+\sigma]$ something between pure $[\sigma+\sigma]$ and $[q^--q^-]$. This is not unreasonable, since our practical $[s+s]$ is always (by definition) nearer to the pure $[s+s]$ than to the pure $[\sigma+\sigma]$, and so on. It might be contended that it would be better to use the symbols $[q^++q^+]$ etc. appropriate to 50–50 mixing whenever these represent better approximations than pure forms $[s+s]$ etc. That is, for mixtures in the range between 75, 25 and 25, 75 proportions, we might use the $[q\pm q]$ symbols, reserving $[s\pm s]$ and $[\sigma\pm\sigma]$, respectively, for mixtures between 0, 100 and 25, 75, and between 75 25 and 100, 0. The difficulty is that in practise we usually are not yet sure whether or not the actual proportions in a given case come within the 75, 25 to 25, 75 range; and furthermore, our symbolism would suffer unnecessary complication in trying to make the distinction.

With the foregoing understanding as to symbolism we return to (7) to note that the distribution of $C-H$ and $C-C$ bonding power among the practical orbitals $[s+s]$, $[s-s]$, and $[\sigma+\sigma]$ varies according to the degree of $s-p\sigma$ mixing. The forms of *pure* $[s+s]$, $[s-s]$, and $[\sigma+\sigma]$ are such that pure $[s+s]$ is (probably strongly) $C-C$ bonding and at the same time (probably weakly) $C-H_2$ bonding; $[s-s]$ is $C-C$ antibonding ($C\leftrightarrow C$) but may be strongly $C-H_2$ bonding; $[\sigma+\sigma]$ is mainly $C-C$ bonding but has some $C-H_2$ bonding power. Hybridization

between $[s+s]$ and $[\sigma+\sigma]$ should alter their relative $C-C$ and H_2-C bonding powers, probably increasing the $C-C$ and decreasing the $C-H_2$ for $[s+s]$ with the reverse effect for $[\sigma+\sigma]$.

Understanding of the structure of C_2H_4 is helped by considering its formation from 2 CH_2.[13a, 11] To get (7) with *pure* $[s+s]$ etc., two excited CH_2 radicals are needed, each in the condition

$$[sa_1]^2[yb_2]^2[za_1](2p_xb_1), \quad ^{1, 3}B_1. \qquad (8)$$

To get (7a), we should need two CH_2 radicals in an artifically constructed excited condition

$$[q^-a_1]^2[q^+a_1][yb_2]^2[2p_xb_1], \quad ^{1, 3}B_1. \qquad (8a)$$

For the actual (7), with impure $[s+s]$ etc., something between (8) and (8a) is needed; or, practically, the symbols $[sa_1]$ and $[za_1]$ in (8) may be understood to be mutually contaminated forms.

Lennard-Jones[14] has described the process of putting a radical (e.g., here CH_2) into an artificially constructed state, suited to the condition of the radical when combined, as "reorganization." The proper reorganized state to be used comes under the heading of "valence states,"[3b] a term introduced by Van Vleck. The proper valence state here has not only to be intermediate between pure (8) and (8a), but also between the $^1B_1$ and $^3B_1$ condition, although nearer the latter (cf. discussions of the valence states of atoms[3b]). As a result of the reorganization of the normal state of CH_2 to get the proper valence state, there is some readjustment of the relative $C-H$ bonding powers of $[sa_1]$ and $[za_1]$ as compared with normal CH_2.

Prediction of I's is rather difficult for C_2H_4. The CH_2 orbital $[yb_2]$ is essentially the same as the $[y]$ component[1] of the degenerate orbital $[\pi e]$ of CH_3 in C_2H_6, CH_3X, or CH_4 and, although the charge distribution in its environment is considerably different here than in those cases, it still seems probable that I is about the same as there, i.e., about 14.5 volts. For $[\sigma+\sigma]$ the predicted I depends on how strong the hybridization is with $[s+s]$. For zero hybridization, the

predicted value would be about 12 volts as in C_2H_6. Hybridization would presumably tend to diminish this, yet increased $C-H$ bonding would apparently tend the other way, by partly removing $[\sigma+\sigma]$ from between the negatively charged C atoms. For $[x+x]$ we predict $I > I^\circ(2p_x)_C$, i.e., $I > 11.2$ volts,[3] subject to correction for charge-transfer effects (polarities $H_2{}^+C^-C^-H_2{}^+$). Roughly estimating the charge-transfer correction on I° as -1.5 and the magnitude of the inequality sign as $+1.5$ volts, we arrive at about 11 volts for the estimated vertical I of $[x+x]$.

For the experimental I_{min} of C_2H_4 the best value is probably 10.41 volts, obtained by Price from a Rydberg series in the ultraviolet absorption spectrum.[9] This is of course an adiabatic I, and the vertical I must be greater, since from (7) the electron removed can hardly help being a bonding electron. The vertical I might then be about 10.7 or possibly 11 volts, which agrees with the predicted value for $[x+x]$.

The possibility that the observed I belongs to $[\sigma+\sigma]$ rather than $[x+x]$, or that both have nearly the same value, cannot, however, be definitely excluded, since our predictions have a considerable margin of uncertainty. The relatively moderate amount of vibration accompanying Price's Rydberg series bands tends to indicate that the observed I is nearly vertical. This is rather surprising in view of the fact that a bonding electron ($[x+x]$ or $[\sigma+\sigma]$) is removed. Possibly it might be explained if it is the $[\sigma+\sigma]$ which is removed, and if this is only weakly $C-C$ bonding and at the same time moderately strongly $C-H$ bonding, a situation which is conceivable as a result of hybridization between $[s+s]$ and $[\sigma+\sigma]$. Or if it is the $[x+x]$ which is removed, perhaps the resultant weakening of the bond is less pronounced than one would be inclined to expect.

The longest wavelength absorption of C_2H_4 has been attributed in previous papers[11, 13a] to a transition from (7) to an excited state ^1B_u:

$$[x+x]^{-1}[x-x, b_{2g}], \quad ^{3, 1}B_{1u}, \qquad (9)$$

i.e. to a transition of an electron from $[x+x]$ to $[x-x]$.[12a] It is reasonable to expect that the orbital $[x-x]$ is the lowest excited orbital and that it is far from being of a Rydberg series type; it should resemble the x component of the degenerate orbital $(\pi-\pi, \pi_g)$ which is known in O_2.[13a] Another possible excited orbital is $[\sigma-\sigma, b_{1u}]$, but it is probable that this is very high in

14 J. H. Lennard-Jones, Trans. Faraday Soc. **30**, 70 (1934).

energy, and it may resemble a $3p\sigma$ Rydberg orbital, as was suggested above for the similar orbital $[\sigma-\sigma]$ of C_2H_6.

Among others, the following excited states of C_2H_4 might be considered (the $^{-1}$ symbols are relative to (7)):

$$[x+x]^{-1}(3sa_{1g}), \quad ^{1, \; 3}B_{3u};$$
$$[\sigma+\sigma]^{-1}(3sa_{1g}), \quad ^{1, \; 3}A_{1g};$$
$$[\sigma+\sigma]^{-1}[x-x], \quad ^{1, \; 3}B_{2g}; \qquad (10)$$
$$[x+x]^{-1}[\sigma-\sigma], \quad ^{1, \; 3}B_{2g};$$
$$[\sigma+\sigma]^{-1}[\sigma-\sigma], \quad ^{1, \; 3}B_{1u}.$$

The selection rules, however, forbid transitions from the normal state (7) to any of these except the B_{1u} and B_{3u}. The $[\sigma+\sigma]^{-1}[\sigma-\sigma]$, $^{3, \; 1}B_{1u}$ is probably of high energy, so probably need not be considered here for the longer wavelength spectra. This leaves only $[x+x]^{-1}(3sa_{1g})$, $^{1, \; 3}B_u$ as a possible competitor of (9) as upper level of the longest wavelength observed bands.

It was shown in a previous paper[13a] that the assumption of a transition $[x+x]\rightarrow[x-x]$, i.e., (7)$\rightarrow$(9), affords a reasonable explanation of the photochemical transformations $cis\leftrightarrow trans$ which occur in C_2H_4 derivatives on absorption of ultraviolet light. The alternative possibility $[x+x]\rightarrow 3s$, i.e., (7)$\rightarrow[x+x]^{-1}(3s)$, $^{1, \; 3}B_u$ of (10), is found on examination not to afford such an explanation. Hence it seems very probable that the ultraviolet absorption which gives rise to $cis\leftrightarrow trans$ transformations in C_2H_4 derivatives is indeed of the type $[x+x]\rightarrow[x-x]$.

The absorption spectra of the simpler C_2H_4 derivatives[12, 15] show indications of two continuous absorption regions, a weaker one with maximum about $\lambda2150$, a stronger one with maximum near $\lambda1800$. In the simplest derivatives, the "maximum" near $\lambda2150$ appears only as a point of inflection in the absorption curve.[12a]

In C_2H_4 itself[12, 15], the whole absorption is very much weaker. Its appearance indicates, according to Scheibe and Grieneisen,[12] that there are two overlapping systems of bands, the first increasing steadily in intensity from about $\lambda2000$ to perhaps about $\lambda1800$ ($\nu=55,560$), the second starting abruptly with a maximum intensity at

---
[15] J. Stark and collaborators, *Jahrb. der Rad. und Elek.* Vol. 10, 141–188 (1913): C_2H_4, C_2H_2, and derivatives.

$\nu=57,320$. These characteristics indicate a considerable change in molecular dimensions in the first system, little change in the second.[12a]

It seems likely that the first absorption region in C_2H_4 and its derivatives may be associated with $[x+x]\rightarrow[x-x]$, the second with $[x+x]\rightarrow 3s$. Assuming $I_{vert}=$ about 11 volts for $[x+x]$, the $3s$ term value comes out about 4 volts, a fairly reasonable value (cf. CH_4), while the $[x-x]$ term value is somewhat greater.
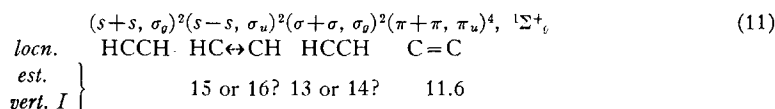
No good reason is evident why the absorption should be so much weaker in C_2H_4 than in its derivatives, since the transitions considered are allowed by the selection rules both for C_2H_4 and the derivatives. Nor is it clear why there should be a displacement toward shorter wavelengths. Much more work will probably be needed before this and similar problems for other molecules will be solved; and it may be that the interpretations given in the present series of papers will need serious modification in the case of excited states.[12a]

In the foregoing it has tacitly been assumed that the orbitals $[x+x]$, $[\sigma+\sigma]$, $[x-x]$, $3s$ are nearly the same, and obey the same selection rules, in C_2H_4 derivatives as for C_2H_4 itself. This is probably true, except for probably weak transitions violating the rather strict selection rules of C_2H_4, since the orbitals mentioned, except perhaps $[\sigma+\sigma]$, are fairly well localized in the neighborhood of the $C=C$ bond. This neighborhood should usually not be very much affected by changes elsewhere in the molecule. The situation is, however, altered seriously in the case of conjugated double bonds or unsaturated rings, which have been discussed by others. Also in the case of C_2H_4 derivatives in which atoms or radicals have been introduced (e.g., I, Br, NH_2) which have nonbonding orbitals of low I, the latter may of course cause new absorption bands to appear in the same region as the $[x+x]\rightarrow[x-x]$ bands or even at longer wavelengths.

IV. ACETYLENE

The normal state of acetylene (symmetry $D_{\infty d}$ like the isoelectronic molecule N_2) may be described, omitting carbon $1s$, as

$$(s+s, \sigma_g)^2(s-s, \sigma_u)^2(\sigma+\sigma, \sigma_g)^2(\pi+\pi, \pi_u)^4, \quad {}^1\Sigma^+_g \qquad (11)$$

locn.　　HCCH　HC↔CH　HCCH　　C = C

est. ⎫
vert. I ⎬　　　　　15 or 16? 13 or 14?　　11.6

The electron configuration given by (11) is formally identical with that for N_2,[3a] except for a probable reversal of the energy order of $(\sigma+\sigma)$ and $(\pi+\pi)$. The main differences as compared with N_2 are connected with the C−H bonding properties of the σ orbitals. These arise because the latter, in LCAO approximation, are linear combinations, not of pure C atom orbitals $2s$ or $2p\sigma$, but of certain σ orbitals of CH (see below) which already involve C−H bonding, being themselves, in LCAO approximation, combinations of $1s_H$ with C atom orbitals. The $(\pi+\pi)$ orbital, on the other hand, is built from practically pure $2p\pi$ of carbon.

The very close approach of the two CH radicals in C_2H_2 (cf. Table I) should cause a very large difference in I between $(s+s)$ and $(s-s)$. The strong interaction should also bring about marked $s-p\sigma$ hybridization, i.e., strong mixing between $(s+s)$ and $(\sigma+\sigma)$, both of which are σ_g, and again between $(s-s)$ and the (excited) orbital $(\sigma-\sigma)$, both σ_u. This mixing should tend to increase the I of $(s+s)$ and of $(s-s)$, to decrease those of $(\sigma+\sigma)$ and $(\sigma-\sigma)$. Quite possibly the mixing is so strong that it would be a better approximation to write

$$(q^+ + q^+, \sigma_g)^2(q^- - q^-, \sigma_u)^2(q^- + q^-, \sigma_g)^2$$
$$\times (\pi+\pi, \pi_u)^4, \quad {}^1\Sigma^+_g \quad (11a)$$

instead of (11). At any rate, something between (11) and (11a) should be correct. For the sake of simplicity, we may in practice use (11) to represent this intermediate condition, by letting the symbols $(s+s)$, $(s-s)$, $(\sigma+\sigma)$ imply not pure $(s+s)$ etc. but partially mixed forms, just as we did in the case of the similar symbols for C_2H_4 (cf. discussion following Eq. (7a)).

The molecular orbital indicated in LCAO approximation by $(q^+ + q^+)$ would give very strong C−C bonding and simultaneous weak C−H bonding, $(q^- - q^-)$ weak C−C antibonding and strong C−H bonding, $(q^- + q^-)$ weak C−C bonding and strong C−H bonding. The relations for pure $(s+s)$, $(s-s)$, and $(\sigma+\sigma)$ are similar, but differ in the distribution of bonding strengths,

particularly in that pure $(s-s)$ should give strong C↔C antibonding.

Light is thrown on the structure of C_2H_2 not only by comparing it with N_2, but also by examining its relationship to CH+CH. The configuration (11) or (11a) can be thought of as derived by bringing together two CH radicals each in a suitable "reorganized" valence state (cf. discussion of CH_2+CH_2 following Eq. (8a) above). The proper reorganized state for pure (11) would be a certain mixture of the four states

$$1s^2 2s\sigma^2(1s_H+2p\sigma, \sigma)2p\pi^2, \quad {}^4\Sigma^-, \; {}^2\Sigma^+, \; {}^2\Delta, \; {}^2\Sigma^-. \; (12)$$

For (11a) it would be a mixture of the four states

$$1s^2(2q^-\sigma+1s_H,\sigma)^2 2q^+\sigma 2p\pi^2,$$
$$\qquad\qquad {}^4\Sigma^-, \; {}^2\Sigma^+, \; {}^2\Delta, \; {}^2\Delta^-. \quad (12a)$$

The symbol $2s\sigma$ used in (12) indicates small participation in the C−H bonds, which is probably correct for the free CH radical. Similarly in (12a), $(2q^+\sigma)$ is nearly but not entirely free from C−H bonding. Insofar as (12a) is needed for the formation of actual C_2H_2, the reorganization from (12) toward (12a) involves an increased participation of $2s\sigma$ (as part of $2q^-\sigma$) in the C−H bonds.

The fact that C_2H_2 acts as a weak acid indicates that there is a considerable net positive charge on each H atom, more so than in C_2H_4 or C_2H_6. This may well be connected with a reluctance of the carbon $2s$ electrons to enter into C−H homopolar bonds, because their natural I is so much greater than that of $1s$ of H. The importance of this effect is greater here than in C_2H_4 and especially C_2H_6, because a larger fraction of the C−H bonding is here taken care of by orbitals which (in LCAO approximation) are built up from carbon $2s$ orbitals.

Because of uncertainty as to the extent and effect of $s\sigma-p\sigma$ hybridization, and of $2s↔2s$ resonance, estimates of I's for the σ orbitals in (11) are decidedly uncertain. If we follow the usual rules and methods,[2, 3] a good prediction can, however, be made for $(\pi+\pi, \pi_u)$, which is localized in the C−C bond region. We have

$$I(\pi+\pi) > I^\circ(2p\pi),$$

where $I^\circ(2p\pi)$ for carbon is 10.86 volts, as determined in the usual way.[3] [This value differs a little from the value 11.23 volts for $2p\sigma$ and from the value 11.21 volts used for $2p_x$, $2p_y$ and $2p_z$ $=2p\sigma$ in discussing C_2H_4.] Allowing $+2.5$ volts for the inequality sign (cf. the corresponding case of N_2,[3a] where the inequality is $+2.8$ volts for $(\pi+\pi)$), and -1.5 volts as an estimate of the effect of the net negative charge on the carbons (polarities $H^+C^-C^-H^+$), one arrives at a prediction of about 11.9 volts for I of $(\pi+\pi)$.

The best experimental value of I for C_2H_2 probably is 11.35 volts, that obtained by Price from two Rydberg series. This is supported by a recent electron impact value 11.2 volts[16] (Morris[10] got 12.2). A comparison with our estimated I's makes it probable that the electron ionized is $(\pi+\pi)$, although the possibility $(\sigma+\sigma)$ or even $(s-s)$ cannot thereby be entirely excluded in view of the uncertainties as to the exact nature of these. Price's I is of course an adiabatic value; since a bonding electron is removed, the vertical I should be larger, but probably not much larger since only one $C-C$ bonding electron out of six is removed. The fact that Price's Rydberg series bands are shaded toward the red indicates an increased moment of inertia in the upper states, in agreement with what we expect for excitation of a bonding electron. A reasonable guess for the vertical I would be 11.6 volts, in good agreement with our estimate given above for $(\pi+\pi)$.

We may next seek to interpret the observed ultraviolet absorption spectra of C_2H_2, namely, the relatively very weak band system $\lambda2400$–1900,[15, 17] and the Rydberg series of Price. According to Kistiakowsky, each band has a double head, presumably a Q and an R head, in which case the upper level is probably of type $^1\Pi_u$. Jonesco, however, using high resolution, finds that the bands (or at least several of them) have only P and R branches, with alternating intensities, exactly as expected if they are $^1\Sigma^+_g\rightarrow{}^1\Sigma^+_u$. This work also shows that the molecule is linear in the excited state, and that the moment of inertia is somewhat greater than in the normal state.

There appears to be some doubt, however, and some disagreement between Kistiakowsky and Jonesco, in regard to the vibrational analysis and the relative intensities of the bands. If the resultant vibrational states involved in the bands analyzed by Jonesco should be other than of the most symmetrical (Σ_g) type, then we could not conclude from the band structure that the electron transition is $^1\Sigma^+_g\rightarrow{}^1\Sigma^+_u$. The presence of vibrations of types ν_1 and ν_2, which are both of symmetry σ_g, also even certain combinations or harmonics of ν_3, ν_4, ν_5 (respectively of symmetry types σ_u, π_u and π_g), would, however, not invalidate the conclusion that the upper state is $^1\Sigma^+_u$, which on the whole seems the most probable. A possibility, however, suggested by the weakness of the bands, is that the electron transition is of a forbidden type.[11a] For certainty, a more complete analysis will be needed.

If the upper level of the $\lambda2200$ bands is $^1\Sigma^+_u$, this must probably be the $^1\Sigma^+_u$ of

$$(\pi+\pi, \pi_u)^{-1}(\pi-\pi, \pi_g),\ ^{3,}\ ^1\Sigma^+_u,\ ^{3,}\ ^1\Sigma^-_u,\ ^{3,}\ ^1\Delta_u.\ (13)$$

This assumption yields a term value of about 5 or 5.5 volts for $(\pi-\pi)$. If, however, the upper level should be $^1\Pi_u$, this must probably be $^1\Pi_u$ of

$$(\pi+\pi, \pi_u)^{-1}(3s\sigma_g),\ ^{1,\ 3}\Pi_u.\ (14)$$

Here, similarly to C_2H_4 and C_2H_6, $3s$ corresponds to $(3s_{CH}+3s_{CH}, \sigma_g)$. The term value of 5 or 5.5 volts appears rather too high for $3s$, and the low intensity of the bands (only about $1/100{,}000$ as strong as the Rydberg series bands according to Price) tends against this possibility. On the whole, it appears very probable that (13) rather than (14) is correct. That $(\pi-\pi)$ should be the lowest excited orbital of C_2H_2 is in harmony with what is known about the excited orbitals of N_2, NO, O_2 and C_2H_4. That the transition $(\pi+\pi)\rightarrow(\pi-\pi)$, involved in going from the normal state to $^1\Sigma^+_u$ of (13), is very weak is in agreement with what is known of the N_2 spectrum, and with the low intensity of $[x+x]\rightarrow[x-x]$ in C_2H_4.

As for Price's Rydberg series bands, the presence of probably only R heads in one series (I) gives evidence that here the upper electron levels are of Σ^+ type, presumably $^1\Sigma^+_u$, while the presence of double heads, presumably Q and R, in the other (II) indicates that there they are of Π type, presumably $^1\Pi_u$. It appears doubtful, however, that we can count on these results without a more detailed analysis, especially since it is stated that all the observed bands of each series

[16] J. T. Tate, P. T. Smith and A. L. Vaughan, Phys. Rev. 43, 1054 (1933).

[17] G. B. Kistiakowsky, Phys. Rev. 37, 277 (1931); G. Herzberg, Trans. Faraday Soc. 27, 379 (1931). A. Jonesco, Comptes rendus 199, 710 (1934); 200, 817 (1935).

have the same kind of heads, a result which is inconsistent with the vibrational analysis given by Price.

Tentatively accepting the evidence for $^1\Sigma^+_u$ and $^1\Pi_u$ states, however, the following possibilities of explanation are available:

$$\text{Series I:} \quad {}^1\Sigma^+_u \text{ of } (\pi+\pi,\ \pi_u)^{-1}(nx\pi_g),\ {}^{3,\ 1}\Sigma^+_u,\ {}^{3,\ 1}\Sigma^-_u,\ {}^{3,\ 1}\Delta_u. \tag{15}$$

$$\text{Series II:} \quad {}^1\Pi_u \text{ of } (\pi+\pi,\ \pi_u)^{-1}(nx\sigma_g),\ {}^{3,\ 1}\Pi_u \text{ or of } (\pi+\pi,\ \pi_u)^{-1}(nx\delta_g),\ {}^{3,\ 1}\Pi_u,\ {}^{3,\ 1}\Gamma_u$$

The only likely possibility for the excited orbital $nx\pi_g$ of series I is $nd\pi_g$ ($n = 3,\ 4,\ \cdots$ for the observed bands). Now as Price points out, the λ2200 bands fit very well, so far as frequency is concerned, as $n = 2$ of series I. This may well be significant, since the LCAO form $(\pi - \pi)$ in (13) closely resembles the atomic orbital $3d\pi$; it seems reasonable that $(\pi - \pi)$ may take the place of $3d\pi$, and so fit in as the first member of the $nd\pi$ series (the n numbering given by Price must then be increased by one). The low intensity for the λ2200

bands as compared with the others would then be somehow connected with the fact that $(\pi - \pi)$, unlike the other $nd\pi$, is not mostly outside the core. The existence of this sort of distinction is supported by empirical evidence in various other cases.

For series II the possibilities $ns\sigma_g$ or $nd\sigma_g$ and $nd\delta_g$ may be considered, with $nd\sigma$ ($n = 3,\ 4,\ 5,\ \cdots$) the most likely; the term values are not reasonable for ns.