Calculation on the Changes of Vibrational Frequencies due to Electronic Excitation in Several Organic Molecules

By Tosinobu ANNO*, Akira SADÔ and Ikuo MATUBARA

(Received April 4, 1956)

Introduction

In the vibrational analysis of the electronic spectrum it is important to know the correspondence between the vibrational frequencies in the ground electronic state and those in the excited state. This correspondence together with the Franck-Condon principle enables one to know about the change of the shape and dimension of the carrier molecule caused by an electronic excitation. This correspondence has hitherto been determined on the basis of the empirical facts found in similar molecules. To contribute a theoretical basis to this problem, a method will be proposed and will be applied to benzene, mesitylene, 1, 3, 5-trichlorobenzene and *p*-dichlorobenzene. The method is of the first approximation, as will be discussed later, but it can explain the frequency changes at least qualitatively.

Method of Calculation

The essential idea of the present method is that the bond-order is calculated by the empirical LCAO MO method for the two electronic states and the bond-length is deduced from the bond-order bond-length relation. Badger's relation[1,2] is used to calculate the stretching force constant, and the deformation force constant is deduced from a rather well established frequency. These force constants are then used to calculate the vibrational frequencies in the valence-force-field approximation.

Excepting the mesitylene molecule, the calculation of the orbital coefficients in the LCAO form was performed with the assumptions described elsewhere[3]. In the case of mesitylene, only the hyperconjugation perpendicular to the plane of the benzene ring was taken into account, assuming that the coulomb integral of the quasi H_3 "atom" is equal to the coulomb integral of the carbon atom in benzene[4], and that the resonance integral of $C{\equiv}H_3$ bond is equal to 4.83 times the resonance integral of the C–C bond in benzene[5]. The definition of the bond-order is the same as that of Coulson and Longuet-Higgins[6].

Bond-lengths were deduced from bond-orders with the help of Coulson's curve[7] for C–C bonds, taking into account the effect of hybridization[8]. For C–Cl bonds the order-length curve due to Anno and Sadô[3] was used with an appropriate modification which takes account of the effect of hybridization of carbon σ-atomic orbital only.

---

* Department of Chemistry, College of General Education, Kyushu University, Fukuoka.

T.A. is greatly indebted to the Dean of the Faculty of Science and Professor S. Imanishi for permitting him to continue his work in the Faculty.

1) R.M. Badger, *J. Chem. Phys.* **2**, 128 (1934).

2) R.M. Badger, *J. Chem. Phys.* **3**, 710 (1935).

3) T. Anno and A. Sadô, This Bulletin, **28**, 350 (1955).

4) R.S. Mulliken, C.A. Rieke and W.G. Brown, *J. Am. Chem. Soc.* **63**, 41 (1941).

5) Mulliken et al. (ref. (4)) took the resonance integral β^* of the $C \equiv H_3$ bond equal to 4.06 times the β_{CC} at $r = 1.33$ Å. Since β_{CC} in benzene ($r = 1.39$ Å) is 0.84 times β_{CC} at 1.33 Å according to Mulliken, we took $\beta^* = (4.06/0.84)\beta_{benzene} = 4.83\beta_{benzene}$.

6) C.A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London), **A191**, 39 (1947).

7) C.A. Coulson, *Proc. Roy. Soc.* (London) **A169**, 413 (1939).

8) C.A. Coulson, "Victor Henri Memorial Volume", Meson Desoer, Liège (1948), p. 15.

Badger's relation[1,2] of the following form was used to obtain the stretching force constant from the above-obtained values of bond-length:

$$r_e=(C/k_e)^{1/3}+d, \tag{1}$$

where r_e and k_e are the equilibrium distance and the force constant of the bond, respectively, and C and d are constants. The physical meaning proposed by Badger[1] for d is that it represents the most approachable distance of the atom pair. It varies considerably from pair to pair. The meaning of C is not obvious. It remains rather constant as compaired with d. In fact Badger took it as a universal constant in the first paper of his series[1]. In Fig. 1 the inverse third power of the force constants of C–C bonds in several molecules are plotted against bond-lengths. In the same figure a line (b) is drawn through the point for benzene with the slope of $(1.86)^{1/3}$ (this is equal to the value of $C^{1/3}$ taken as a universal constant in Badger's first paper[1]) and it is seen that the line passes through the point for ethylene. If we draw straight lines parallel to the line b through points for acetylene and ethane, two lines a and c are obtained, which cut the r_e-axis at 0.717 and 0.798 Å, respectively, while the line b cuts the same axis at 0.765 Å. These values may be considered to represent three different d-values for C–C bond corresponding to three different states of hybridization of carbon atoms (a, b, c correspond to sp, sp^2, sp^3, respectively). Since Coulson[8] has shown that the carbon atom takes different covalent radii depending on its state of hybridization, it may be considered that this causes the change of the most approachable distance in the C–C bonds in the respective states of hybridization. If this is correct, the d-values for carbon atom pairs corresponding to sp, sp^2 and sp^3 hybridizations should have a sequence $d(\text{sp-sp})<d(\text{sp}^2\text{-sp}^2)<d(\text{sp}^3\text{-sp}^3)$. This is actually the case for lines a, b and c in Fig. 1. For this reason we assume that the relation (1) holds, where C is a universal constant but d may have different values depending upon the species and the states of hybridization of the participating atoms.

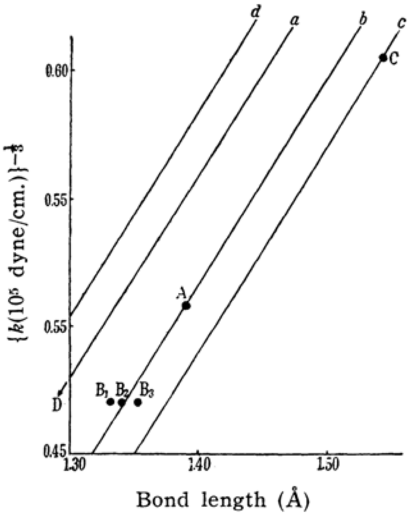

Fig. 1. Badger's rule for the C–C bonds.

a Drawn parallel to line d through the point for acetylene (not shown in the figure).

b Drawn parallel to line d through the point for benzene.

c Drawn parallel to line d through the point for ethane.

d From Badger's original paper (reference 1).

$$r=(1.86/k)^{\frac{1}{3}}+0.68$$

A: Benzene
($r=1.39$ Å[a], $k=7.61\times10^5$ dyne/cm.[b]).
B$_1$: Ethylene
($r=1.331$ Å[c], $k=9.57\times10^5$ dyne/cm.[d]).
B$_2$: Ethylene
($r=1.340$ Å[e], $k=9.57\times10^5$ dyne/cm.[d]).
B$_3$: Ethylene
($r=1.353$ Å[f], $k=9.57\times10^5$ dyne/cm.[d]).
C: Ethane
($r=1.543$ Å[g], $k=4.50\times10^5$ dyne/cm.[h]).
D: Acetylene
($r=1.207$ Å[i], $k=15.80\times10^5$ dyne/cm.[j]).

a V. Schomaker and L. Pauling, *J. Am. Chem. Soc.*, **61**, 1769 (1939).
b F. M. Garforth, C. K. Ingold and H. G. Pool, *J. Chem. Soc.*, **1948**, 491.
c H. W. Thompson, *Trans. Faraday Soc.*, **35**, 697 (1939).
d G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand Co. Inc., New York (1945) p. 184.
e C. A. Coulson, "Victor Henri Memorial Volume", Meson Desoer, Liège, (1948) p. 15.
f W. S. Gallaway and E. F. Barker, *J. Chem. Phys.*, **10**, 88 (1942).
g G. H. Hansen and D. M. Dennison, *J. Chem. Phys.*, **20**, 313 (1952).
h Reference d p. 193.
i Reference d p. 398.
j Reference d p. 180.

In Fig. 2 the inverse third power of the force constants and the bond-lengths of the C–Cl bonds in chloroacetylene and methyl chloride are plotted as in Fig. 1 for C–C bonds. The straight lines a and c passing through the points for chloroacetylene and methyl chloride, respectively, are drawn with the slope of $1.86^{1/3}$ (see above). The line a gives a smaller d-value than the line c. This difference may result from the difference of the state of hybridization of the carbon atom. The state of hybridization of the carbon atom attached to the chlorine atom in chlorobenzenes is undoubtedly the intermediate of those in chloroacetylene and methyl chloride. Unfortunately, since we have neither the

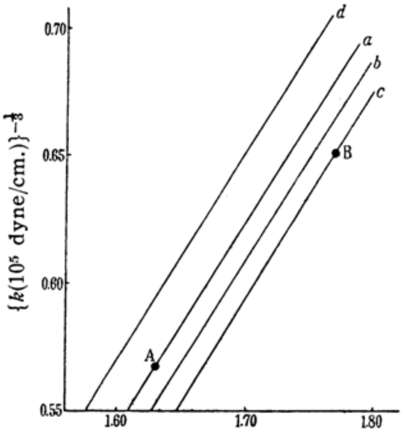

Fig. 2. Badger's rule for the C–Cl bonds.

a Drawn parallel to line *d* through the point for chloroacetylene.

b Drawn parallel to line *d* and at the middle of lines *a* and *c*.

c Drawn parallel to line *d* through the point for methyl chloride.

d From Badger's original paper (reference 1).

$$r=(1.86/k)^{\frac{1}{3}}+0.900.$$

A: Chloroacetylene ($r=1.63$ Å[a], $k=5.52\times10^5$ dyne/cm.[b]).

B: Methyl chloride ($r=1.77$ Å[a], $k=3.64\times10^5$ dyne/cm.[c]).

[a] Landolt-Börnstein, "Zahlenwerte und Funktionen", Springer, Berlin, (1951).

[b] W. S. Richardson and J. H. Goldstein, *J. Chem. Phys.*, 18, 1314 (1950).

[c] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand Co. Inc., New York (1945) p. 193.

precise knowledge of the hybridization of the carbon atoms in these molecules nor the quantitative knowledge about the variation of the *d*-values as a function of the state of hybridization, the line *b*, which we use throughout this paper, is drawn just in the middle of the lines *a* and *c*. Our conclusion may be little affected by the arbitrariness of drawing the line *b*, since we are concerned only with the change of vibrational frequencies in the two electronic states of a particular molecule, and not with the calculation of the absolute values of the vibrational frequency themselves.

Furthermore, we assume implicitly that the states of hybridization of the atoms are not affected by the electronic excitation. Briefly, we deduce the force constants from the calculated bond-lengths using the lines *b* of Figs. 1 and 2 for C–C and C–Cl bonds, respectively, both for the ground and the excited electronic states.

Bond-order, Bond-length and Bond-force-constant

The calculated values of bond-order, bond-length, and bond force-constant are shown in Tables I and II for the ground and the first excited states, respectively. Numberings of atoms are shown in Fig. 3. One thing should be mentioned in regard to the calculations for the first excited states of benzene, mesitylene and 1, 3, 5-trichlorobenzene. It can be shown that the first excited states of these molecules are accidentally degenerate and single configurations do not represent the excited states for these molecules even when the configurational interaction is neglected, because the wave functions corresponding to single configurations do not form the bases of the irreducible representations of the

TABLE I

CALCULATED VALUES OF BOND-ORDERS, BOND-LENGTHS, AND BOND-FORCE-CONSTANTS IN THE GROUND ELECTRONIC STATES

Molecule	Bond	Total bond-order	Bond-length (in Å)	Bond-force-constant (in 10^5 dyne/cm.)
Benzene	C_1–C_2	1.667	1.390	7.61
Mesitylene	C_1–C_2	1.661	1.390	7.61
	C_1–C_1'	1.125	1.498	5.05
1, 3, 5-Trichlorobenzene	C_1–C_2	1.635	1.395	7.40
	C_1–Cl_1	1.320	1.687	4.68
p-Dichlorobenzene	C_1–C_2	1.633	1.395	7.45
	C_2–C_3	1.675	1.388	7.70
	C_1–Cl_1	1.298	1.691	4.60

TABLE II

CALCULATED VALUES OF BOND-ORDERS, BOND-LENGTHS, AND BOND-FORCE-CONSTANTS IN THE FIRST EXCITED STATES

Molecule	Bond	Total bond-order	Bond-length (in Å)	Bond-force-constant (in 10^5 dyne/cm.)
Benzene	C_1–C_2	1.500	1.416	6.75
Mesitylene	C_1–C_2	1.497	1.415	6.79
	C_1–C_1'	1.138	1.496	5.08
1, 3, 5-Trichlorobenzene	C_1–C_2	1.523	1.413	6.90
	C_1–Cl_1	1.334	1.684	4.73
p-Dichlorobenzene	C_1–C_2	1.555	1.407	7.04
	C_2–C_3	1.481	1.418	6.68
	C_1–Cl_1	1.472	1.665	5.11

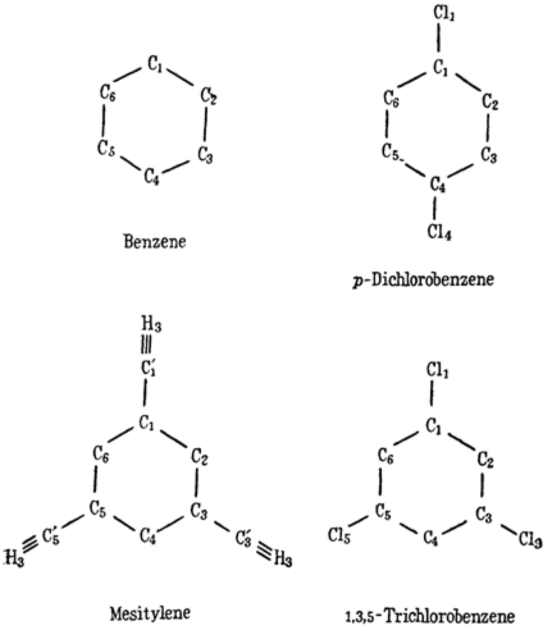

Fig. 3

point groups appropriate to these molecules. But it is easy to obtain, by linearly combining the configurational functions, the wave functions which do form the bases of the irreducible representations of the molecular point groups. These combinations involve only two configurational functions, which differ from each other in the assignment of two electrons so that the bond-orders for the states result only from superpositions of the participating configurations. Thus, the bond-order is found to be the same in the accidentally-degenerate first-excited states of particular one of these molecules.

Calculation of Vibrational Frequencies

In this paper we shall confine ourselves to the totally symmetrical skeleton vibrations since these appear more prominently in UV spectra for those molecules treated in the present paper than the other types of vibration.

Benzene.—For the benzene molecule the value of the C–C stretching force constant is only required to calculate the totally symmetrical skeleton vibrational frequency. The results are shown in Table III. Since the ground-state value is used to establish the line *b* in Fig. 1, the corresponding calculated value is in brackets. Comparison of the calculated values with the observed ones will be discussed later.

TABLE III

CALCULATED AND OBSERVED VALUES OF TOTALLY SYMMETRICAL SKELETON VIBRATIONAL FREQUENCY OF THE BENZENE MOLECULE

		Calculated	Observed[a]
Ground state (cm^{-1})	A_{1g}	(993)	992
Excited state (cm^{-1})	B_{2u}	937	923
	B_{1u}	937	965
	E_{1u}	937	—
Drop(%)[b]	A_{1g}–B_{2u}	5.6	7.0
	A_{1g}–B_{1u}	5.6	2.7
	A_{1g}–E_{1u}	5.6	—

a Taken from reference 14 and 15 in text.

b $\text{Drop}(\%)=\dfrac{\nu_{(\text{G.S.})}-\nu_{(\text{E.S.})}}{\nu_{(\text{G.S.})}}\times 100.$

Mesitylene, 1, 3, 5-Trichlorobenzene and *p*-Dichlorobenzene.—In the case of the mesitylene molecule as well as other molecules than benzene, the totally symmetrical skeleton-vibrational frequencies are determined not only by bond-stretching force constants but also by bending force constants. These bending force constants come into the secular equation for each molecule as the combination of only one kind among them. So, one vibrational frequency for each molecule is sufficient to determine the value of the combination of bending force constants, and the other frequencies may be calculated. The results are shown in Table IV. The frequencies used for calculating deformation force constants are in brackets. The choice of the frequency from which the value of the deformation force constant was calculated was made on the basis of the following two conditions:

(i) Assignment of the frequency must be certain.

(ii) The corresponding vibrational mode must be mainly of deformation, in which case a large change in frequency yields only a small change in deduced deformation force constant, or a combination of such constants.

The first singlet-singlet absorption spectrum of mesitylene has been analyzed by Sponer and Stallcup[9]. There seems to be no question in correlating the 968- and 555-cm^{-1} frequencies in the upper state with the 997- and 575-cm^{-1} ground-state values, respectively. They obtained as an upper-state frequency 1300 cm^{-1} and correlated it with the observed Raman shift of 1299 cm^{-1} rather than the alternative one of 1378 cm^{-1}. The former correlation gives a frequency drop by −0.1%, while the latter gives a drop of 5.7%. Sponer and Stallcup preferred the former, commenting that it is not improbable for the corresponding vibrational frequencies in the two electronic states to have nearly

---

[9] H. Sponer and M. J. Stallcup, Ref. (8), p. 222.

TABLE IV

CALCULATED AND OBSERVED VALUES OF TOTALLY SYMMETRICAL SKELETON VIBRATIONAL FREQUENCY OF THE MESITYLENE, 1, 3, 5-TRICHLOROBENZENE, AND *p*-DICHLOROBENZENE MOLECULES (THE FORCE CONSTANTS USED IN CALCULATION ARE TAKEN FROM TABLE I AND II)

		Calculated			Observed^a		
		G. S.(cm^{-1})	E. S.(cm^{-1})	Drop(%)^b	G. S.(cm^{-1})	E. S.(cm^{-1})	Drop(%)^b
Mesitylene	ν_1	1427	1422	0.4	1299	1300	−0.1
	ν_2	(997)	(968)	—	997	968	2.9
	ν_3	571	537	6.0	575	555	3.5
1, 3, 5-Trichlorobenzene	ν_1	1351	1332	1.4	1146	1122	2.1
	ν_2	(995)	(963)	—	995	963	3.2
	ν_3	365	360	1.4	375	369	1.6
p-Dichlorobenzene	ν_1	1675	1584	5.4	1589	1461/66	8.1/7.8
	ν_2	1186	1166	1.7	1102	1051	4.6
	ν_3	(755)	(725)	—	755	725	4.0
	ν_4	275	241	12.4	331	244	26.3

a a Taken from: mesitylene, reference 9; 1, 3, 5-$C_6H_3Cl_3$, reference 10, *p*-$C_6H_4Cl_2$, reference 11, in text.

b See footnote b in Table III.

the same values. According to our calculation the drop amounts to 0.4%, in favor of the correlation by Sponer and Stallcup.

The UV absorption spectrum of 1, 3, 5-trichlorobenzene was studied by Sponer and Hall⁽¹⁰⁾. In this case, the correlations of the 963- and 1122-cm^{-1} upper-state frequencies with the 995- and 1146-cm^{-1} ground-state values seem to be certain. The frequency difference of 369 cm^{-1} found in UV spectrum was correlated with the 375-cm^{-1} ground-state value with some reservations. This correlation gives only a small drop of 1.6%, which is not impossible according to Sponer and Hall. The present calculation shows this drop to be 1.4%.

The vibrational analysis of the longest wave length singlet-singlet absorption of *p*-dichlorobenzene was carried out by Anno and Matubara⁽¹¹⁾. There can be no doubt in correlating 725 and 1051 cm^{-1} in the excited state with 755 and 1102 cm^{-1} in the ground state. It is reported there that the upper-state frequency corresponding to the 331-cm^{-1} ground-state value may be taken as 244 cm^{-1}, the 331-cm^{-1} frequency being considered as an alternative. The former choice gives a drop of 26.3%, while the latter would give no drop at all. The present calculation gives a drop of 12.4%, in favor of Anno and Matubara's analysis. To the remaining upper-state frequency 1461/66 cm^{-1} the ground-state frequency 1589 cm^{-1} may correspond. It is not certain which component of the band gives the fundamental frequency in the excited electronic state. This correlation gives a drop of 8.1/7.8%. The present calculation gives a drop of 5.4%.

Discussion

The calculated values of bond-order are naturally affected by the assumed values of the coulomb and resonance integrals. Anno and Sadô have recently found the best values of α_{Cl} and β_{CCl} by fitting the calculated shift of the UV spectrum of *p*-dichlorobenzene with experiment and the calculated value of the π-electron loss at the chlorine atom in vinyl chloride with quadrupole coupling data⁽¹²⁾. These values of α_{Cl} and β_{CCl} are also consistent with the experimental data for other chlorinated hydrocarbons. They have also found that the order-length relation holds as well on the basis of these values of α_{Cl} and β_{CCl}, and the relative calculation of C–Cl bond-length from the bond-order is little affected, whether we use these new values of α_{Cl} and β_{CCl} or whether we make the previously described assumption⁽³⁾. In order to show the effect of the assumed values of α_{Cl} and β_{CCl} on the changes of the vibrational frequencies of chlorinated benzenes, the calculated values of bond-order, bond-length and force constants for *p*-dichlorobenzene and 1, 3, 5-trichlorobenzene are listed in Table V. It may be seen in the table that the changes of the force constants for 1, 3, 5-trichlorobenzene are nearly the same as those given in

---

10) H. Sponer and M.B. Hall, Ref. (8), p. 211.

11) T. Anno and I. Matubara, *J. Chem. Phys.*, **23**, 796 (1955).

12) T. Anno and A. Sadô, To be published in *J. Chem. Phys.*, July (1956).

TABLE V

CALCULATED VALUES OF BOND-ORDERS, BOND-LENGTHS, AND BOND-FORCE-CONSTANTS FOR 1, 3, 5-TRICHLOROBENZENE AND *p*-DICHLOROBENZENE BASED ON α_{Cl} AND β_{CCl} DERIVED FROM EXPERIMENTAL DATA (SEE TEXT).

		Ground states			First excited states		
Molecule	Bond	Total bond-order	Bond-length (in Å)	Bond-force-constant (in 10^5 dyne/cm.)	Total bond-order	Bond-length (in Å)	Bond-force-constant (in 10^5 dyne/cm.)
1, 3, 5-Trichlorobenzene	C_1–C_2	1.626	1.396	7.42	1.548	1.408	7.02
	C_1–Cl_1	1.242	1.686	4.69	1.256	1.683	4.75
p-Dichlorobenzene	C_1–C_2	1.647	1.393	7.54	1.495	1.416	6.76
	C_2–C_3	1.670	1.388	7.72	1.515	1.413	6.87
	C_1–Cl_1	1.230	1.688	4.65	1.367	1.664	5.15

Tables I and II. As for *p*-dichlorobenzene the changes of the force constants are somewhat different from those listed in Tables I and II. Therefore we have calculated the vibrational frequencies of *p*-dichlorobenzene from the force constants given in Table V in the same manner as described previously. The results are given in Table VI. The calculated values of the changes of the frequency are in accordance with the values listed in Table IV at least qualitatively.

TABLE VI

CALCULATED AND OBSERVED VALUES OF TOTALLY SYMMETRICAL SKELETON VIBRATIONAL FREQUENCY OF *p*-DICHLOROBENZENE (THE STRETCHING FORCE CONSTANTS USED IN CALCULATION ARE TAKEN FROM TABLE V).

		Calculated			Observed[a]		
		G. S. (cm^{-1})	E. S. (cm^{-1})	Drop (%)[b]	G. S. (cm^{-1})	E. S. (cm^{-1})	Drop (%)[b]
p-Dichlorobenzene	ν_1	1677	1587	5.4	1589	1461/66	8.1/7.8
	ν_2	1190	1173	1.4	1102	1051	4.6
	ν_3	(755)	(725)	—	755	725	4.0
	ν_4	272	250	8.1	331	244	26.3

a Taken from reference 11 in text.
b See footnote b in Table III.

It is implicitly assumed in the present calculation that the molecules have planar configurations in both the electronic states. All molecules treated here have undoubtedly planar structures in their electronic ground states (treating each H_3 "atom" in mesitylene as a mass point). The vibrational analysis shows that these molecules seem also to be planar in their first excited electronic states, in which we are interested.

As to the effect of configurational interaction (CI) we are considering the case of the benzene molecule only, as for obvious reasons it is difficult at present to estimate such an effect in other molecules.

The effect of CI on the energy levels of the benzene molecule is well known. Unfortunately, however, the coefficients of mixing of different configurations are not found in the literature except for the ground A_{1g}- and the lowest E_{1u}-states of this molecule[13]. Therefore, we must be content with qualitative considerations. We hope to have another opportunity to discuss this effect more quantitatively.

Our calculated values of bond-orders for benzene are correct in so far as CI is neglected, and are independent of the method of calculation (e. g. simple LCAO MO, anti-

TABLE VII

LOWER SINGLET LEVELS OF THE BENZENE MOLECULE CALCULATED WITH AND WITHOUT CONFIGURATIONAL INTERACTION (eV.).

Level	Roothaan and Parr[a]	Parr, Craig and Ross[b]	Observed[c]
$^1A_{1g}$	0.0	0.0	0.0
$^1B_{1u}$	7.3	9.0	6.0
$^1B_{2u}$	5.9	4.4	4.9
$^1E_{1u}$	9.8	9.9	7.0

a) Configurational interaction is neglected. All the integrals are included. (*J. Chem. Phys.*, **17**, 1001 (1949)).
b) Configurational interaction and all the integrals are included. (*J. Chem. Phys.*, 18, 1561 (1950)).
c) Taken from Pariser and Parr, *J. Chem. Phys.*, **21**, 767 (1953).

---

[13] C.W.L. Bevan and D.P. Craig, *Trans. Faraday Soc.*, **47**, 564 (1951). In this paper many-center integrals are neglected.

symmetrized products of molecular orbitals with or without many center integrals, etc.). However, CI produced by the higher energy configurations in which the C–C bonds have smaller bond-orders should decrease the bond-orders in the original configuration. It is to be noted that the bond-orders even in the ground state should more or less decrease. However, as can be seen in Table VII, the magnitudes of the energy changes produced by CI fit in the following sequence:

$$B_{2u}>A_{1g}\approx E_{1u}>B_{1u}.$$

If the same sequence applies to the bond-order changes, we can expect that for A_{1g}–B_{2u} or A_{1g}–B_{1u} transitions the bond-order decrease caused by the electronic excitation may be greater or smaller than when the CI is neglected, while for A_{1g}–E_{1u} transition it may be nearly the same, whether CI is considered or not. The same applies to the totally symmetrical ringvibrational frequency. Thus we can expect that the above-calculated value of 937 cm^{-1} should represent the upper and the lower limit for the vibrational frequency in the B_{1u}- and B_{2u}-state, respectively. The observed values are 923 and 965 cm^{-1} for the B_{2u}- and B_{1u}-state, respectively[14,15].

Errors due to Badger's relation appear to be small. As for the effect of d-values it may not be serious in calculating the change of the frequency caused by the electronic excitation as described above. The effect of C-values may have to be considered even for the calculation of the frequency change. According to Badger's second paper[2], this constant varies among atom pairs with the maximum deviation of 10%, which results in the error of 30% in the difference of the force constants. Therefore, the error in the frequency difference is estimated to be less than 20%.

Errors due to the valence-force-field (VFF) approximation are difficult to estimate. According to Wilson[16] the following equation holds:

$$\Lambda=L^{-1}GFL=L'FL, \tag{2}$$

where Λ is a diagonal matrix whose diagonal elements are the characteristic roots of the secular equation $|GF-E\lambda|=0$. G is the inverse kinetic energy matrix and F is the force constant matrix. L is the transformation matrix defined by

$$R=LQ,$$

where R and Q represent the internal and normal coordinates, respectively, prime and reciprocal denoting the transpose and the inverse matrices, respectively. In the case of the symmetrical molecules, each symmetry type can be treated separately, and in such cases R represents the symmetry coordinate formed by an appropriate linear combination of the equivalent internal coordinates. Taking the ii element of Eq. (2) it follows that

$$\lambda_i=\sum_{k,m}(L')_{ik}F_{km}L_{mi}=\sum_{k,m}L_{ki}L_{mi}F_{km}. \tag{2'}$$

From this equation the first order change of λ_i produced by small changes of F_{km}'s is given by

$$\delta\lambda_i=\sum_{k,m}L_{ki}L_{mi}\delta F_{km}. \tag{3}$$

Now, from Eqs. (2′) and (3) the relative change of λ_i is

$$\frac{\delta\lambda_i}{\lambda_i}=\frac{\sum\limits_{k,m}L_{ki}L_{mi}\delta F_{km}}{\sum\limits_{k,m}L_{ki}L_{mi}F_{km}}$$

$$=\frac{\sum\limits_{k}L_{ki}L_{ki}\delta F_{kk}+\sum\limits_{k,m\neq k}L_{ki}L_{mi}\delta F_{km}}{\sum\limits_{k}L_{ki}L_{ki}F_{kk}+\sum\limits_{k,m\neq k}L_{ki}L_{mi}F_{km}}. \tag{4}$$

The use of the VFF approximation implies that in the last expression of Eq. (4) the second sums in the denominator and numerator can be neglected as compared with the corresponding first sums. In order to investigate the error due to the VFF approximation, four cases may be considered.

(i) If λ_i refers to the characteristic frequency of the stretching internal coordinate R_k, it holds that[17]

$$\lambda_i\approx(L_{ki})^2F_{kk}.$$

In general, for planar vibrations the magnitude and the change are greater for stretching force constants than those for deformation force constants and interaction constants[18]. Therefore,

$$\delta\lambda_i\approx(L_{ki})^2\delta F_{kk}.$$

Accordingly, the error due to the VFF approximation does not seem to be serious in this case.

(ii) If λ_i refers to the characteristic frequency of two (or more) stretching internal coordinates R_k and R_l, it holds that[17]

$$\lambda_i\approx(L_{ki})^2F_{kk}+(L_{li})^2F_{ll}+2(L_{ki}L_{li})F_{kl},$$

where the first and the second terms of the right hand side are of the same order of

---

[14] H. Sponer, G. Nordheim, A. L. Sklar and E. Teller, *J. Chem. Phys.*, 7, 207 (1939).

[15] G. Nordheim, H. Sponer and E. Teller, *J. Chem. Phys.*, 8, 455 (1940).

[16] E. B. Wilson, Jr., *J. Chem. Phys.*, 7, 1047 (1939); 9, 76 (1941).

[17] Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, 20, 1809 (1952).

[18] J. Duchesne, *J. Chem. Phys.*, 21, 548 (1953), 22, 1464 (1954), *Bull. Acad. Roy. Belg.*, 39, 697 (1953), *J. phys. radium*, 15, 211 (1954), *Acad. Roy. Belg., Classe sci. Mem. Collection in* 8°, 28, 3 (1955) and J. Duchesne and L. Burnelle, *J. Chem. Phys.* 21, 2005 (1953).

magnitude. From considerations similar to those in the previous case

$$\delta\lambda_i \approx (L_{ki})^2 \delta F_{kk} + (L_{li})^2 \delta F_{ll} + 2(L_{ki}L_{li})\delta F_{kl}.$$

Taking into account the fact that the magnitude and the change are greater for stretching force constants than those for bond-bond interaction constants it follows that

$$\frac{\delta\lambda_i}{\lambda_i} \approx \frac{(L_{ki})^2\delta F_{kk} + (L_{li})^2\delta F_{ll} + 2(L_{ki}L_{li})\delta F_{kl}}{(L_{ki})^2 F_{kk} + (L_{li})^2 F_{ll} + 2(L_{ki}L_{li}) F_{kl}}$$

$$\approx \frac{(L_{ki})^2\delta F_{kk} + (L_{li})^2\delta F_{ll}}{(L_{ki})^2 F_{kk} + (L_{li})^2 F_{ll}},$$

in which the relative error in the frequency change due to the second approximation may be of the same order of magnitude as the relative error due to the VFF approximation in the calculation of the absolute values of vibrational frequency.

(iii) If λ_i refers to the characteristic frequency of the deformation internal coordinate R_δ, it holds that[17)]

$$\lambda_i \approx (L_{\delta i})^2 F_{\delta\delta}.$$

In general, the magnitude and the change of the in-plane deformation force constants are small and are comparable with those of the interaction constants. Therefore, it is doubtful whether the following approximation holds fairly well:

$$\delta\lambda_i \approx (L_{\delta i})^2 \delta F_{\delta\delta}.$$

In addition, in the method described in the present paper, various effects due to interaction constants are included in $F_{\delta\delta}$ when it is deduced form the experimental frequency. Furthermore, if we use this value of $F_{\delta\delta}$ in calculating another vibrational frequency the error included may be great, since the contributions from interaction constants to the latter frequency may be different from the contributions to the frequency from which $F_{\delta\delta}$ is calculated. Therefore, the error due to the VFF approximation is expected to be great in this case.

(iv) If λ_i refers to the characteristic frequency of the deformation (R_δ) and stretching (R_k) internal coordinates,

$$\lambda_i \approx (L_{\delta i})^2 F_{\delta\delta} + (L_{ki})^2 F_{kk} + 2(L_{\delta i}L_{ki}) F_{\delta k},$$

where the first and the second terms in the right hand side are nearly equal in magnitude. The error due to the VFF approximation is expected to be great also in this case on account of the error in $F_{\delta\delta}$ as described above.

Thus, it may be concluded that the use of the VFF approximation does not produce serious errors for the vibration whose mode is almost bond-stretching.

To summarize although the present approach to the problem of the changes of the vibrational frequencies in the course of the electronic excitation involves many sources of error, the results obtained are encouraging at least qualitatively. In other words, the present calculation cannot be expected to predict precisely the frequency changes in these molecules, but it is of some use in understanding or interpreting the observed frequency changes.

Finally, we express our sincere thanks to Professor S. Imanishi for his encouragement throughout this work and for his kindness in reading the manuscript.

Department of Chemistry, Faculty of
Science, Kyushu University
Fukuoka