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Virginia Griffing

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The Size and Vibration Frequency of the Excited Benzene Molecule*

VIRGINIA GRIFFING
The Catholic University of America, Washington, D. C.
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It is shown that the change in size and vibration frequency of a polyatomic molecule upon electronic excitation can be calculated if the excitation energy is known as function of the distance. This is applied to benzene, for which this function is calculated both with the Heitler-London-Slater-Pauling method and the molecular orbital method. Upon comparison with experiment, it is found that both methods give the right sign and order of magnitude for the change in size, but the wrong sign for the change in frequency.

I. INTRODUCTION

THIS paper is an attempt to connect the resonance energy—considered as a function of the distance between atoms—in a polyatomic molecule with the change of its size and vibration frequency caused by electronic excitation.

Consider first a diatomic molecule. If one plots the binding energy as function of the distance, the minimum of the curve gives the size of the molecule, the curvature gives the restoring force, and, therefore, the frequency of the vibration.

If one can calculate the electronic excitation energy as a function of the nuclear distance, and can add this to the energy of the ground state taken from experiment, one gets, as a function of the distance, the energy of the excited state, and from it the size of the excited molecule and its vibrational frequency.

The same argument can be applied to a

polyatomic molecule of sufficient symmetry that it has a "breathing" vibration, in which it can be characterized by a single distance.

This idea will be applied here to molecules having resonance, in particular to benzene—in which excitation consists in a transition to a state differing from the ground state only by resonance splitting.

It is then generally assumed that the in-plane bonds are not affected by excitation, i.e., the energy curve of the ground state is the sum of two energy curves, that of the in-plane bonds and that of the ground state of the π-bonds. Similarly, the energy curve of the excited state is given by the sum of the energy curves of the unmodified in-plane bonds and of the excited π-bonds.

The difference between the energy curves of the excited state and of the ground state as function of the distance—from which the change in the size of the molecule and the change in frequency of the breathing vibration can be calculated—is therefore equal to the excitation energy of the resonance π-bonds as function of the distance.
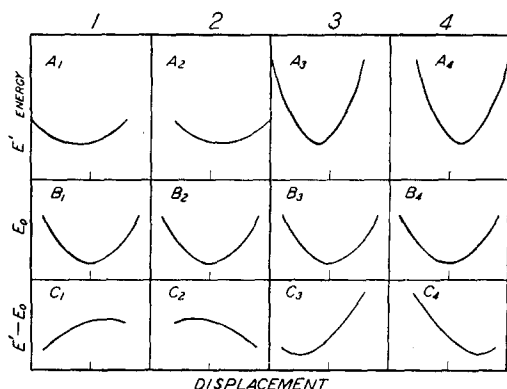
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FIG. 1. The four possible excitation energy curves (C) as function of the distance; the energy of the ground state, (B); the energy of the excited state (C). Case I, the excited molecule is smaller and has lower frequency. Case II, the excited molecule is larger and has lower frequency (e.g., benzene). Case III, the excited molecule is smaller and has higher frequency. Case IV, the excited molecule is larger and has higher frequency.

II. DISCUSSION OF THE FORM OF POSSIBLE FUNCTIONS

Consider a polyatomic molecule in its vibrationless ground state. Assume that this state is perturbed by a symmetrical breathing vibration that is characterized by a displacement $(R-R_0)$, of the atoms from an equilibrium position R_0. Call n the number of significant bonds which partake in resonance excitation and are stretched in the breathing vibration ($n=6$ for benzene, $n=N-1$ for a polyene with N carbon atoms). If the breathing vibration is of small amplitude then the energy of this state can be written

$$E(R) = E_0(R_0) + \tfrac{1}{2}nK(R-R_0)^2, \quad (1)$$

where E_0 is the energy of the vibrationless ground state, and K is the force constant whose magnitude is determined from the frequency of vibration. The validity of this approximation can be checked experimentally by the constancy of the frequency differences between the members of a sequence of vibration bands. In the excited state both the size of the molecule and the force constant may have changed so that the energy is written

$$E'(R) = E_1(R_1) + \tfrac{1}{2}nK'(R-R_1)^2. \quad (2)$$

R_1 is the equilibrium position and K' the force constant in the excited state.

In polyatomic molecules it is often impossible to calculate $E_0(R_0)$ and $E_1(R_1)$ separately, but if

one calls $E_1(R_1) - E_0(R_0) = U_0$, U_0 is independent of R and is the energy of an electronic transition from the vibrationless ground to the vibrationless excited state. Then the excitation energy $\Delta E(R)$ as function of R can be written

$$\begin{aligned} \Delta E(R) &= E'(R) - E(R) \\ &= U_0 + \tfrac{1}{2}nK'(R-R_1)^2 - \tfrac{1}{2}nK(R-R_0)^2. \end{aligned}$$

Now if $R_0 = R_1 - \delta$ then

$$\begin{aligned} \Delta E(R) = U_0 &- nK'\delta[R - (R_0+R_1)/2] \\ &+ \tfrac{1}{2}n(K'-K)(R-R_0)^2. \quad (3) \end{aligned}$$

Furthermore,

$$(d\Delta E(R)/dR) = n(K'-K)(R-R_0) - nK'\delta,$$

that is, in the region of vibration of very small amplitude when $(R-R_0)$ is small, the slope of the curve representing the excitation energy is determined by the change in the equilibrium distance. Therefore, the change in the size of the molecule upon excitation is given by

$$\delta = -\frac{n}{K'}\left[\frac{d\Delta E}{dR}\right]_{R_0} = -\frac{n}{K}\left[\frac{d\Delta E}{dR}\right]_{R_1}. \quad (4)$$

According to the definition of curvature

$$L = \frac{d^2\Delta E/dR^2}{[1+(d\Delta E/dR)^2]^{\frac{3}{2}}}. \quad (5)$$

Since the denominator is always positive, the sign of the curvature is the same as the sign of $d^2\Delta E/dR^2$. Specifically, the curvature is positive (concave upward) if $(K'-K)$ is positive as is the case when the force constant is larger in the excited than in the ground state. The curvature is negative (concave downward) if $(K'-K)$ is negative, i.e., the frequency of the vibration is smaller in the excited than in the ground state.

The four possible cases are shown in Fig. 1. Curves A_n (Eq. 2) are the potential energy curves for the excited state. Assume the same curve B (Eq. 1) in the four cases for the ground state. C_n (Eq. 3) shows the difference $(B-A)$, namely, the excitation energy.

Case I—$K > K'$, $R_0 > R_1$. This is the case of a molecule that is smaller in the excited than in the ground state and the restoring force, thus the frequency of vibration is smaller in the excited state. Therefore, for vibrations of small amplitude the excitation energy can be represented by

a quadratic curve with a positive slope and negative curvature as shown in C_1, Fig. 1.

Case II—$K > K'$, $R_0 < R_1$. This represents a molecule that is larger in the excited state while the force constant is smaller in the excited state. For this case the excitation energy gives a quadratic curve with negative slope and negative curvature (C_2, Fig. 1).

Case III—$K < K'$, $R_0 > R_1$. In this case the molecule is smaller and the frequency of vibration larger in the excited state. The excitation energy is represented by a quadratic curve with positive curvature and positive slope (C_3, Fig. 1).

Case IV—$K < K'$, $R_0 < R_1$. This is a molecule that is larger and has a larger frequency of vibration in the excited than in the ground state. The excitation energy (C_4, Fig. 1) is represented by a quadratic curve with negative slope and positive curvature.

For cases where $K = K'$, the excitation energy is represented by a straight line; if $R = R_0$ it is horizontal. Therefore, given a method of accurately determining the excitation energy of symmetrical polyatomic molecules as a function of a characteristic coordinate, it is possible to determine the change in size of the molecule from the slope of the curve and the change in the frequency of the symmetrical vibration from the curvature.

In general the excitation energy of a polyatomic molecule might be represented by a curve such as shown in Fig. 2. This curve approaches a constant value as the distance between the atoms becomes very large. The numbers in Fig. 2 show in what part of the general excitation energy curve one finds sections having one of the four different shapes just discussed. In what part of the excitation energy curve the ground state equilibrium dimension R_0 will fall is, of course, determined by the energy curve of the ground state as function of the distance and therefore strongly influenced by the in-plane bonds.

III. EXPERIMENTAL DATA FOR BENZENE

Benzene is a polyatomic molecule with a high degree of symmetry in both the ground (E_0) and the first excited (E_{2s}) state. A detailed analysis of the absorption spectra of benzene in the region of 2600A has been made by Sponer,
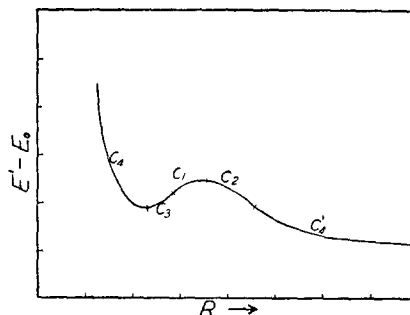

FIG. 2. The general form of excitation energy as function of a characteristic distance.

Nordheim, Sklar, and Teller.[1] In this analysis the totally symmetrical breathing vibrations of both the C−C and C−H bonds have been identified in both the ground and excited state, and the change in the size of the molecule is estimated. These quantities taken from reference 1 are tabulated in Table I along with the force constants that will be discussed below:

TABLE I.

	C−C frequency cm^{-1}	C−H frequency cm^{-1}	C−C force constant dynes 10^6 cm	ev (R units)^2	C−C equilibrium distance A	R units
Ground state	992	3062	7.603	1.3138	1.400	8.37
Excited state	923	2565	6.602	1.1408	1.418	8.49

Wilson[2] has discussed the possible vibrations of a mechanical system of mass points such as benzene and has calculated the frequencies of the totally symmetrical breathing vibration in terms of simple potential functions involving only the force constants of the C−C and C−H bonds. Following Wilson[2] and making use of the frequencies given in Table I, the C−C force constants as given in Table I were calculated. These force constants are for vibrations of small amplitude about the equilibrium positions.

The values of the force constants and equilibrium positions from Table I are substituted in Eq. (3) and the value of $U_0 = 5$ ev taken from Sklar,[3] so that the excitation energy of the first electronic shift found by experiment can be written**

[1] H. Sponer, G. Nordheim, A. L. Sklar, E. Teller, J. Chem. Phys. **7**, 207 (1939).
[2] E. B. Wilson, Jr., Phys. Rev. **45**, 706 (1934).
[3] A. L. Sklar, J. Chem. Phys. **5**, 669 (1937).
** $0.5190 = 6 \times \frac{1}{2}(1.3138 - 1.1408)$.

$$E_{2s} - E_0 = 5.000 - 0.8214(R - R_0)$$
$$- 0.5190(R - R_0)^2, \quad (6)$$

where $E_{2s} - E_0$ is in electron volts and R/Z is the C−C distance in atomic units. $Z = 3.18$ is the effective charge of a neutral carbon atom as determined by Zener.[4]

The experimental value of 38089 wave numbers (or 4.71 electron volts) for the zero-zero band does not only contain the energy of the electronic jump, but also the differences of the zero-point energies of all vibrations in the excited state and the ground state. However, this difference in zero-point energies will surely not exceed 10 percent of the corresponding electronic energies, and since in our comparison we are not concerned with a high accuracy, that will be neglected. The use of 5 ev in the place of 4.71 enters the calculation of the dependence on R only in one place (Section IV c), where a factor 0.4636 is used to fit the theoretical and experimental values together at the equilibrium position.

Thus according to experiments as interpreted in reference 1, benzene is an example of Case II, Section II. In other words, the molecule is larger and the vibration frequency is lower in the excited than in the ground state; the C−C distance increases about 1.5 percent, and the vibration frequency decreases about 7 percent.

According to Sklar[5] the frequency of the breathing vibration in the E_{1s} level (in the region of 2000A) is still about 920 cm⁻¹. The spectroscopic data in this region have not been sufficiently analyzed to estimate the shift in the C−C distance.

IV. THEORETICAL TREATMENT OF BENZENE

(a) General Considerations

Sklar[3] has calculated the electronic states of benzene according to the Heitler-London-Slater-Pauling (HLSP) method. The same problem has been considered according to the method of antisymmetrized molecular orbitals by Goeppert-Mayer and Sklar[6] (hereafter referred to as GMS paper). There is good agreement between the two

methods in predicting the experimentally observed electronic absorption spectra of benzene in the region of 2600A. The excitation energy used in these discussions is a function of the C−C distance. The numerical evaluations were made only for the experimentally determined C−C equilibrium distance. However, this assumption does not enter in principle into the calculations. Therefore, it is the purpose of this section to extend both of these theoretical treatments to the calculation of the excitation energy for a small range of R in the region of the equilibrium position. This corresponds to two independent theoretical determinations of the excitation energy as a function of R. From these it should be possible to predict the change in frequency of the totally symmetric C−C vibration and the change in the size of the benzene molecule in the excited state.

Both methods have the following assumptions in common. According to Hückel[7] the charge distribution associated with each carbon atom in the benzene ring can be considered thus: Two inner electrons are considered to be on the nucleus and the remaining four electrons are valence electrons; three of the valence electrons are represented by sp^2 hybridized wave functions in the plane of the ring; the fourth, a $2p\pi$ electron, is described by a $2p\pi$ wave function with its node in the plane of the ring and the charge distribution perpendicular to the ring so that there is little overlap with the electrons forming the in-plane bonds. Thus the two sets of electrons can be considered independently, and only the six $2p\pi$ electrons concern us. It is assumed that excitation to the excited states considered here does not affect the in-plane bonds at all, except insofar as the distance between atoms is changed. Consequently this is a six electron problem with the hexagonal symmetry of the benzene ring. All interactions, except coulomb, of electrons between particles farther apart than neighbors are neglected.

(b) Notations

The following notations used in this paper are slightly different from those of the GMS paper.

H the Hamiltonian operator of the benzene molecule, including the repulsion between electrons.

[4] C. Zener, Phys. Rev. **36**, 51 (1930).
[5] A. L. Sklar, Rev. Mod. Phys. **14**, 232 (1942).
[6] M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. **6**, 645 (1938).
[7] E. Hückel, Zeits. f. Physik **70**, 204 (1931).

$K(\nu)$ the $2p\pi$ wave function of the Kth carbon atom.

i.e., $I(\nu)$, $II(\nu)$, $\cdots VI(\nu)$.

$\nu, \mu = 1 \cdots 6$ denote the six $2p\pi$ electrons.

S_{V+1} the overlap integrals

$$\int K(\nu)[K+V](\nu)d\tau_\nu.$$

α single exchange integral between neighbors for the benzene molecule.

E_0 energy of the ground state.

E_{ns} energy of the nth singlet electronic state.

R/Z the $C-C$ distance in atomic units.***

Z = the effective nuclear charge for a neutral carbon atom.

$R_0 = 8.37$, i.e., the equilibrium distance of t C$-$C nuclei in benzene in the ground state.he

I ionization energy of a carbon atom in the valence state (taken as negative).

τ_ν volume of space in terms of the coordinates of electron ν.

The atomic coulomb integrals

$$A_N = \int \int \frac{e^2}{r_{\nu\mu}} K^2(\nu)[K+N]^2(\mu)d\tau_\nu d\tau_\mu.$$

The atomic mixed exchange and coulomb integral

$$B_{12} = \int \int \frac{e^2}{r_{12}} I^2(1)I(2)II(2)d\tau_1 d\tau_2.$$

The atomic exchange integral

$$C_{12} = \int \int \frac{e^2}{r_{12}} I(1)II(1)I(2)II(2)d\tau_1 d\tau_2.$$

The atomic penetration integrals

$$Q = -\int H_I(\nu)K^2(\nu)d\tau_\nu,$$

$$T = -\int H_I(\nu)K(\nu)[K+I](\nu)d\tau_\nu \,(R \text{ in GMS}),$$

where H_I is the attraction of a neutral carbon atom in the valence state for the electron ν.

ϵ_l energy of the lth molecular orbital caused by the potential of the benzene ring.

*** R is called ρ by Sklar and Lyddane in reference 8.

The coulomb integrals between molecular orbitals

$$\gamma_{ll'} = \int \int \frac{e^2}{r_{\nu\mu}} |\phi_l(\nu)|^2 |\phi_{l'}(\mu)|^2 d\tau_\nu d\tau_\mu.$$

The exchange integrals between molecular orbitals

$$\delta_{ll'} = \int \int \frac{e^2}{r_{\nu\mu}} [\phi_l(\nu)\phi_{l'}(\mu)][\phi_l(\mu)\phi_{l'}(\nu)]^* d\tau_\nu d\tau_\mu,$$

where

$$\phi_l(\nu) = (6\sigma_l)^{-\frac{1}{2}} \sum_{k-1}^{6} \exp\frac{2\pi ilk}{6} K(\nu),$$

the lth molecular orbital and σ_l = normalization coefficients.

(c) The Heitler-London-Slater-Pauling Method

Using the simplified HLSP method Sklar[3] showed that the energies of the five different electronic states were due to resonance splitting of the five homopolar structures without including any polar structures. Thus he was able to express the energy difference between the ground and the excited states in terms of the single exchange integral, α, which is defined by the following equation

$$\alpha = \int \int \int \int \int \int I(1)II(2)III(3)IV(4)$$

$$\times V(5)VI(6)HI(2)II(1)III(3)$$

$$\times IV(4)V(5)VI(6)d\tau_1 d\tau_2 d\tau_3 d\tau_4 d\tau_5 d\tau_6. \quad (7)$$

For the energy difference between the ground and the lowest electronic state Sklar obtained the following:

$$E_{2s} - E_0 = -2.6\alpha. \quad (8a)$$

Sklar did not calculate the value of α but used an experimental thermochemical value of the resonance energy (1.11α) to obtain the energy difference given in his paper. Since H is a function of R, α was calculated as a function of R from (7)

$$\alpha = C_{12} - S_1 \left\{ 4T + 2B_{12} + S_1 \left[6Q + 6A_1 + 5A_2 \right. \right.$$

$$\left. \left. + 3A_3 - 6I - \frac{6Z}{R}(1 + \tfrac{1}{3} + \tfrac{1}{4}) \right] \right\}. \quad (9a)$$

The numerical values of the integrals occurring in

TABLE II. The HLSP method.

C—C distance A	R units	a $\alpha - 6S_1{}^2 I$	b α (Eq. 9a)	c $E_{2s} - E_0$	d $E_{2s} - E_0$ (Eq. 8c)
1.484	8.87	−1.7599 ev	−2.9916 ev	3.6061 ev	3.7150 ev
1.450	8.67	−2.0448	−3.4219	4.1248	4.1294
1.433	8.57	−2.2033	−3.6579	4.4092	4.3868
1.417	8.47	−2.3748	−3.9110	4.7143	4.6765
1.400	8.37	−2.5571	−4.1788	5.0371	5.0001
1.383	8.27	−2.7589	−4.4706	5.3889	5.3667
1.367	8.17	−2.9624	−4.7677	5.7470	5.7471
1.333	7.97	−3.4938	−5.5014	6.6314	6.6275
1.300	7.77	−4.1057	−6.3343	7.6354	7.6413

Eq. (9) as a function of R are given in the appendix of this paper. Although it was known that this approximate calculation would not give the correct absolute value of $E_{2s} - E_0$ it was hoped that the relative variation with R would be reliable. $(\alpha - 6S_1{}^2 I)$ was first calculated because the estimated value of I was not very reliable. These values are listed in Table IIa. α as a function of R calculated by this equation for an estimated value of I is given in Table IIb.

In order to discuss the results conveniently the best quadratic equation to fit the numbers in Tables IIa and IIb was obtained by the method of least squares

$$(\alpha - 6S_1{}^2 I) = -2.5218 + 1.941(R - R_0)$$
$$- 1.162(R - R_0)^2,$$
$$-2.6(\alpha - 6S_1{}^2 I) = 6.5567 - 5.046(R - R_0)$$
$$+ 3.021(R - R_0)^2,$$
$$S_1{}^2 = 0.06754 - 0.03678(R - R_0) + 0.0089(R - R_0)^2.$$

We set I 4 ev as the ionization energy[8] for the carbon atom in the valence state, then

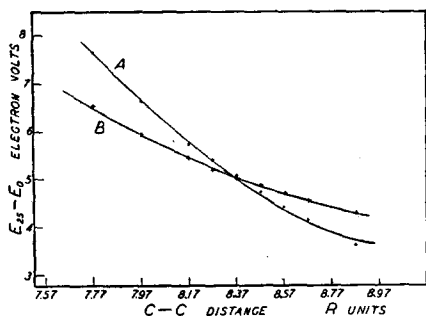$$\alpha = -4.1491 + 2.823(R - R_0)$$
$$- 1.383(R - R_0)^2 \quad (9b)$$

FIG. 3. The excitation energy of benzene $(E_{2s} - E_0)$ as a function of the C—C distance.

[8] J. Duchesne, P. Goldfinger, B. Rosen, Nature 159, 131 (1947).

or

$$E_{2s} - E_0 = -2.6\alpha = 10.7877$$
$$- 7.340(R - R_0) + 3.596(R - R_0)^2. \quad (9c)$$

Adjusting Eq. (9c) to give the correct value for α at $R = R_0$ by multiplying the entire equation by the proper numerical constant, 0.4636, we get

$$E_{2s} - E_0 = 5.000 - 3.402(R - R_0)$$
$$+ 1.667(R - R_0)^2. \quad (8b)$$

In Fig. 3, the curve A was obtained from the quadratic form 8b (see Table IIc). The points are the values obtained by calculation according to Eq. (9a) and multiplication of all values by 0.4636 for the purpose of adjusting these values to fit at $R = R_0$ (Table IIc).

According to Eq. (4) it is possible to calculate the change in the size of the molecule if one knows the experimental value for the force constant in the ground state. A better comparison is with the experimental Eq. (6) which is of the same form as Eq. (8b). From this comparison it can be seen that the calculated change in size has the right sign and is of the right order of magnitude, especially since the experimental value is a rough approximation. However, the frequency shift predicted by this calculation has the wrong sign; i.e., this calculation gives an increase in the force constant and consequently a higher frequency for the totally symmetrical breathing vibration in the excited state. Experiment gives a decrease in frequency of this vibration in the excited state.

(d) Antisymmetrized molecular orbitals

The second method used is an extension to different values of R of the GMS paper, which applies the method of antisymmetrized products of molecular orbitals. The GMS paper expresses the energy as the sum of certain integrals but gives the values of these integrals and of their coefficients only for R_0. The values of these quantities for a range of R are given in the appendix of this paper. Detailed discussion is confined to the first excited level (E_{2s}), which is interpreted as the upper state of the observed band at 2600A. This is the only electronic level for which there is detailed experimental analysis of the structure caused by vibrations. The excitation energy is made up of three parts.

The first part, $(\epsilon_2-\epsilon_1)$, is that part of the energy difference common to all excited states due to the interaction of the electrons with the $2p\pi$-less carbon skeleton and is given by Eq. (31) of the GMS paper

$$\epsilon_2-\epsilon_1=\frac{\dot\sigma_1-\sigma_2}{\sigma_1\sigma_2}\{-2Q-2A_1-2A_2-A_3\}$$

$$+\frac{\sigma_1+\sigma_2}{\sigma_1\sigma_2}\{T+B_{12}\}. \quad (10)$$

The second, $E^1-E_0-(\epsilon_2-\epsilon_1)$ is the interaction caused by the mutual repulsion of the six $2p\pi$ electrons common to all excited states; it is given by Eq. (25) of the GMS paper.

$$E^1-E_0-(\epsilon_2-\epsilon_1)=-2\gamma_{01}+2\gamma_{02}$$
$$-3\gamma_{11}+3\gamma_{12}-\delta_{01}-\delta_{02}+\delta_{1-1}. \quad (11)$$

Now expressing the molecular integrals in terms of atomic integrals according to Eq. (19) of the appendix, Eq. (11) becomes

$$E^1-E_0-(\epsilon_2-\epsilon_1)$$

$$=\left[\frac{1}{6\sigma_0\sigma_1}+\frac{1}{6\sigma_0\sigma_2}-\frac{1}{3\sigma_1\sigma_1}+\frac{1}{2\sigma_1\sigma_2}\right]A_0$$

$$+\left[-\frac{1}{2\sigma_0\sigma_1}+\frac{5}{6\sigma_0\sigma_2}-\frac{7}{6\sigma_1\sigma_1}+\frac{1}{\sigma_1\sigma_2}\right]A_1$$

$$+\left[-\frac{5}{6\sigma_0\sigma_1}+\frac{5}{6\sigma_0\sigma_2}-\frac{7}{6\sigma_1\sigma_1}-\frac{1}{\sigma_1\sigma_2}\right]A_2$$

$$+\left[-\frac{1}{2\sigma_0\sigma_1}+\frac{1}{6\sigma_0\sigma_2}-\frac{1}{3\sigma_1\sigma_1}+\frac{1}{2\sigma_1\sigma_2}\right]A_3$$

$$+\left[-\frac{1}{\sigma_0\sigma_1}+\frac{1}{3\sigma_0\sigma_2}-\frac{5}{3\sigma_1\sigma_1}\right]B_{12}$$

$$+\left[-\frac{1}{6\sigma_0\sigma_1}-\frac{5}{6\sigma_0\sigma_2}+\frac{1}{6\sigma_1\sigma_1}-\frac{1}{2\sigma_1\sigma_2}\right]C_{12}. \quad (11a)$$

The third part is that part of the interaction caused by electron repulsion responsible for the splitting between the various excited states so that the excitation energies are given by Eq. (23) of the GMS paper. Below are given the equations only for the first and second singlet states which

TABLE III. The molecular orbital method.

C–C distance		a	b	c	d
A	R units	$E_{2s}-E_0$ (Eq. 12)	$E_{2s}-E_0$ (Eq. 14)	$E_{1s}-E_0$ (Eq. 13)	$\Sigma_2-\Sigma_1$ (Eq. 10)
1.484	8.87	4.3014 ev	4.3001 ev	5.1220 ev	−4.9302 ev
1.450	8.67	4.5556	4.5439	5.2450	−5.3420
1.433	8.57	4.6898	4.6904	5.3100	−5.5420
1.417	8.47	4.8520	4.8533	5.3940	−5.7347
1.400	8.37	5.0215	5.0326	5.4810	−5.9248
1.383	8.27	5.2073	5.2283	5.5810	−6.1145
1.367	8.17	5.4299	5.4404	5.7130	−6.2791
1.333	7.97	5.9430	5.9138	6.0234	−6.5883
1.300	7.77	6.5350	6.4528	6.3950	−6.8502

are of primary interest in this paper

$$E_{2s}-E_0=(E^1-E_0)+\frac{1}{6\sigma_1\sigma_2}$$

$$\times\{-A_0-2A_2+3A_3+5C_{12}\} \quad {}^1\Gamma_{10}(B_{2u}), \quad (12)$$

$$E_{1s}-E_0=(E^1-E_0)+\frac{1}{6\sigma_1\sigma_2}$$

$$\times\{A_0-6A_1+8A_2-3A_3+C_{12}\} \quad {}^1\Gamma_9(B_{1u}). \quad (13)$$

Equations (12) and (13) are evaluated for a range of R, and the numerical values for these energy differences are given in electron volts in Table IIIa and c. The best quadratic equation (Eq. 14) to represent the numbers in IIIa (Eq. 12) was obtained

$$E_{2s}-E_0=5.0326-1.875(R-R_0)$$
$$+0.8174(R-R_0)^2. \quad (14)$$

The values calculated according to Eq. (14) are given in Table IIIb and are shown in the smooth curve B, Fig. 3, while the points are the calculated points according to Eq. (13), (Table IIIa). No correction factor was used in this case.

Comparing the quadratic Eq. (14) with the experimental Eq. (6), one predicts a change in the size of the molecule that is about twice that estimated from experiment (Eqs. 4, 6, and 14—since the factor of $R-R_0$ is 1.875 against 0.8214—). The change in frequency is of the right order of magnitude but has the wrong sign.

In the following an attempt is made to trace the origin of the difficulty with the curvature. In Fig. 4, curve A is $(\epsilon_2-\epsilon_1)$ (Eq. 10), curve B is $E^1-E_0-(\epsilon_2-\epsilon_1)$ (Eq. 11), and curve C is $E_{2s}-E^1$. The sum of these three curves is the excitation energy $E_{2s}-E_0$, curve D, (Eq. 13) which has already been shown as curve B, Fig. 3. All of these curves are approximately straight
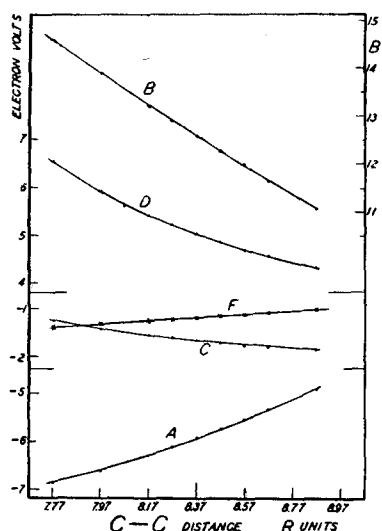
FIG. 4. Curves calculated according to the method of antisymmetrical molecular orbitals.

Curve A: $\epsilon_2 - \epsilon_1$ (Eq. 10)
Curve B: $E^1 - E_0 - (\epsilon_2 - \epsilon_1)$ (Eq. 11)
Curve C: $E_{2s} - E^1$
Curve D: $E_{2s} - E_0(A + B + C)$ (Eq. 12)
Curve F: $E_{1s} - E^1$.

lines except curve A, $(\epsilon_2 - \epsilon_1)$: curve A, therefore, has about the same curvature as the final excitation energy curve. Therefore, any difficulty with the curvature seems to lie with $(\epsilon_2 - \epsilon_1)$; if one inserts numerical values in Eq. (10) (Table IIId) it is found to be negative, although general arguments would point to a higher value of ϵ_2 (energy of the excited orbital) than ϵ_1 (energy of the ground orbital). (This difficulty was pointed out orally to us by A. London.) This makes it appear plausible that the present calculation of $\epsilon_2 - \epsilon_1$ is not accurate enough, both as to absolute value and sign of curvature as function of R.

Curve F shows $E_{1s} - E^1$ and is a straight line just as $E_{2s} - E^1$ (curve C), indicating that the change in frequency of the totally symmetrical vibration in the 2000A band is about the same as in the 2600A band (since $E_{2s} - E_{1s}$ is a straight line). This seems in agreement with the statement (see Section III) that a sequence with wave number difference 920 appears in the 2000A band; this shows that the frequency of the breathing vibration is the same in the E_{2s} and E_{1s} levels. No analysis giving the experimental approximation of the size of the molecule in the E_{1s}

level has been made. The theory (slope of $E_{2s} - E_{1s}$) predicts a change in size of 0.017A in the E_{1s} excited state, if one assumes the experimental value of the force constant $K' = 6.602 \times 10^5$ dynes/cm. Therefore, the molecule is smaller in the E_{1s} than in the E_{2s} level. The theory predicts a change in the $C - C$ distance 53 percent as great as it predicts in the E_{2s} level.

V. DISCUSSION

Experimental data show that the benzene molecule increases in size while the frequency of the breathing vibration decreases by excitation to the lowest electronic excited state. According to the arguments of Section II, the excitation energy as a function of R must have a negative slope and a negative curvature corresponding to Fig. 1c. The calculated curves for the excitation energy both have a negative slope of the right order of magnitude, possibly slightly too large; however, both the HLSP and the MO method give positive curvature (which would mean an increase in the frequency of the breathing vibration in the excited state).

To explain the experimental facts one needs an excitation energy curve of the somewhat peculiar shape shown in Fig. 2.

There are two assumptions which might explain the wrong curvature given by the two theoretical methods. It could be that the force constant of the in-plane bonds is changed in going from the ground to the excited state contrary to the assumption made in both the HLSP and the antisymmetrized molecular orbital methods. Or the assumption that the wave function associated with the $2p$ electrons can be represented by a simple $2p$ wave function with the nuclear charge chosen to give minimum energy for the free carbon atom may be too simple. This assumption is probably sufficiently good in evaluating the coulomb integrals but the overlaps, and consequently the normalization factors and the exchange integrals, are particularly sensitive to the wave function used. A smaller value of the overlap might change the curvature predicted by both methods. A smaller value of the overlap would also give better agreement for the absolute value of the energy difference between theory and experiment in the HLSP method.

It seems worth while to rewrite the calculated

expressions for the excitation energy of the E_{2s} level according to the two methods here for a comparison. The first is according to the HLSP method (Eq. 9 multiplied by -2.6)

$$E_{2s} - E_0 = 2.6C_{12} - 2.6S_1(4T + 2B_{12})$$

$$- 2.6S_1^2\left(6Q + 6A_1 + 5A_2 + 3A_3 - 6I\right.$$

$$\left. - \frac{6Z}{R}\left(1 + \frac{1}{\sqrt{3}} + \frac{1}{4}\right)\right) \quad (15)$$

and the second by the antisymmetrized molecular orbitals (Eq. 12).

$$E_{2s} - E_0 = \frac{\sigma_1 - \sigma_2}{\sigma_1\sigma_2}\{-2Q - 2A_1 - 2A_2 - A_3\}$$

$$+ \frac{\sigma_1 + \sigma_2}{\sigma_1\sigma_2}\{T + B_{12}\}$$

$$+ \left\{-\frac{1}{6\sigma_0\sigma_1} + \frac{1}{6\sigma_0\sigma_2} - \frac{1}{3\sigma_1\sigma_1} + \frac{2}{3\sigma_1\sigma_2}\right\}A_0$$

$$+ \left\{-\frac{1}{2\sigma_0\sigma_1} + \frac{5}{6\sigma_0\sigma_2} - \frac{7}{6\sigma_1\sigma_1}\right\}A_1$$

$$+ \left\{-\frac{5}{6\sigma_0\sigma_1} + \frac{5}{6\sigma_0\sigma_2} - \frac{7}{6\sigma_1\sigma_1} + \frac{14}{6\sigma_1\sigma_2}\right\}A_2$$

$$+ \left\{-\frac{1}{2\sigma_0\sigma_1} + \frac{1}{6\sigma_0\sigma_2} - \frac{1}{3\sigma_1\sigma_1}\right\}A_3$$

$$+ \left\{-\frac{1}{\sigma_0\sigma_1} + \frac{1}{3\sigma_0\sigma_2} - \frac{5}{3\sigma_1\sigma_1}\right\}B_{12}$$

$$+ \left\{-\frac{1}{6\sigma_0\sigma_1} - \frac{5}{6\sigma_0\sigma_2} + \frac{1}{6\sigma_1\sigma_1} - \frac{1}{3\sigma_1\sigma_2}\right\}C_{12}. \quad (16)$$

If one neglects S_2 and S_3 which is consistently assumed in the HLSP method

$$\sigma_0\sigma_1 = 1 + 3S_1 + 2S_1^2, \quad \sigma_0\sigma_2 = 1 + S_1 - 2S_1^2,$$
$$\sigma_1\sigma_2 = 1 - S_1^2, \quad \sigma_1 - \sigma_2 = 2S_1, \quad \sigma_1 + \sigma_2 = 2.$$

Both of these equations are sums of the same atomic integrals multiplied by functions of the overlap integral. In Eq. (15) (HLSP) the ionization energy I of the carbon atom occurs which includes the contribution of the A_0 integral which occurs in Eq. (16) (MO). The kinetic energy included in I and the term

$$\frac{6Z}{R}\left(1 + \frac{1}{\sqrt{3}} + \frac{1}{4}\right)S_1^2,$$

the contribution of the coulomb interaction between the nuclei does not occur in (16). All of the atomic integrals except A_0 occur explicitly in both Eqs. (15) and (16); however, the coefficients are very different. In Eq. (15) the overlap S_1 occurs as a linear and quadratic coefficient while in Eq. (16) the coefficients are of the form

$$\frac{a + bS_1 + cS_1^2}{a' + b'S_1 + c'S_1^2 + d'S_1^3 + e'S_1^4}.$$

The following Table IV shows the numerical value of the coefficients of the atomic integrals in the two expressions for the excitation energy for R equal to R_0, the equilibrium position in the ground state.

ACKNOWLEDGMENTS

TABLE IV.

Atomic integral	Coefficients	
	HLSP	AMO
A_0		0.5982
A_1	1.05408	-1.4653
A_2	0.8784	1.06039
A_3	0.52704	-0.90387
C_{12}	-2.6	-1.07355
B_{12}	1.35174	0.84365
T	2.70348	2.22198
Q	1.05408	-1.11998
I	-1.05408	

TABLE V.

C–C distance A	R units	A_0	A_1	A_2	A_3
1.484	8.87	16.8063 ev	8.643 ev	5.370 ev	4.698 ev
1.450	8.67	16.8063	8.804	5.482	4.798
1.433	8.57	16.8063	8.882	5.543	4.850
1.417	8.47	16.8063	8.964	5.604	4.906
1.400	8.37	16.8063	9.046	5.664	4.958
1.383	8.27	16.8063	9.133	5.725	5.015
1.367	8.17	16.8063	9.215	5.790	5.071
1.333	7.97	16.8063	9.388	5.920	5.188
1.300	7.77	16.8063	9.570	6.054	5.309
notation of reference 9		aa; aa	aa; bb	aa; cc	aa; dd
		B_{12}	C_{12}	Q	T
1.484	8.87	3.651 ev	0.7063 ev	0.5365 ev	1.5204 ev
1.450	8.67	3.950	0.7902	0.6076	1.658
1.433	8.57	4.112	0.8384	0.6461	1.732
1.417	8.47	4.288	0.8925	0.6872	1.810
1.400	8.37	4.478	0.9527	0.7305	1.890
1.383	8.27	4.677	1.0133	0.7786	1.972
1.367	8.17	4.889	1.0800	0.8271	2.069
1.333	7.97	5.365	1.2330	0.9310	2.275
1.300	7.77	5.902	1.4000	1.1272	2.502
notation of reference 9		ab; bb	ab; ab	Q_{22}	Q_{12}

TABLE VI.

C−C distance A	R units	σ_0	σ_1	σ_2	S_1
1.484	8.87	1.5232	1.1852	0.7572	0.2265
1.450	8.67	1.5584	1.1928	0.7422	0.2395
1.433	8.57	1.5767	1.1964	0.7347	0.2462
1.417	8.47	1.5958	1.1999	0.7269	0.2530
1.400	8.37	1.6153	1.2034	0.7189	0.2599
1.383	8.27	1.6356	1.2068	0.7108	0.2671
1.367	8.17	1.6564	1.2101	0.7025	0.2743
1.333	7.97	1.7003	1.2165	0.6852	0.2892
1.300	7.77	1.7469	1.2225	0.6672	0.3047

APPENDIX

The evaluation of the integrals that occur in this paper have been made by Sklar and Lyddane[9] for several values of R. The notation of Sklar and Lyddane is given in parenthesis following the notation used in this paper as defined in Section III(b). It was possible to obtain an interpolation for the atomic coulomb integrals which was good to four significant figures over the range given in Table I of Sklar and Lyddane.

$$A_1(aa;bb) = \frac{2}{R} - \frac{7.528}{R^{2.6}},$$

$$A_2(aa;cc) = A_1(\sqrt{3}R): \quad A_3(aa;dd) = A_1(2R).$$

The exchange integral, C_{12}, $(ab;ab)$, the hybrid coulomb-exchange integral, $B_{12}(ab;bb)$, and the exchange penetration integral, T, (Q_{12}) for atomic orbitals were obtained by extrapolation of curves drawn from the tables of Sklar and Lyddane. The coulomb penetration integral, $Q(Q_{22})$ was calculated in closed form as given by Sklar and Lyddane, Eq. (18). A consistent numerical error was noted in the values given in Table VI of reference 9. The numbers given in their Table VI are larger by a factor 2.34 than those given by their Eq. (18).

The resultant numerical values of the energy integrals occuring in this paper as function of R are given in Table V. The units are electron volts.

The normalization coefficients are defined as in the GMS paper thus:

$$\sigma_l = 1 + 2S_1 \cos\frac{2\pi l}{6} + 2S_2 \cos\frac{4\pi l}{6} + (-1)^l S_3, \quad (17)$$

where S_V are overlaps and were calculated from

the closed form[10]

$$S_1 = \int I(1)II(1)d\tau_1 = \frac{6}{120}\left\{\exp\left(\frac{-R}{2}\right)\right\}$$
$$\times\{(R^3+12R^2+60R+120)\}, \quad (18)$$
$$S_2 = S_1(\sqrt{3}R), \quad S_3 = S_1(2R).$$

The values of the normalization coefficients σ_0, σ_1, σ_2 and the overlap S_1 are given in Table VI.

The general expression for the coulomb and interaction integrals (see GMS) between molecular orbitals is given below. All interactions of electrons, except coulomb, on atoms farther apart than neighbors are neglected.

$$\gamma_{ll'} = \frac{1}{6\sigma_l\sigma_{l'}}\left\{ A_0 + 2A_1 + 2A_2 + A_3 \right.$$
$$+ 4B_{12}\left(\cos\frac{2\pi l}{6} + \cos\frac{2\pi l'}{6}\right)$$
$$\left. + 4C_{12}\left(\cos\frac{2\pi l}{6}\cos\frac{2\pi l'}{6}\right)\right\},$$

$$\delta_{ll'} = \frac{1}{36\sigma_l\sigma_{l'}}\left\{ 6A_0 + 12C_{12} \right.$$
$$+ A_1\left(10\cos\frac{2\pi(l-l')}{6}\right.$$
$$\left.+ 2\cos\frac{10\pi(l-l')}{6}\right) + B_{12}\left(20\cos\frac{2\pi l'}{6}\right. \quad (19)$$
$$\left.+ 20\cos\frac{2\pi l}{6} + 4\cos\frac{10\pi l'}{6} + 4\cos\frac{10\pi l}{6}\right)$$
$$+ C_{12}\left(2\cos\frac{10\pi(l+l')}{6}\right.$$
$$\left.+ 10\cos\frac{2\pi(l+l')}{6}\right) + A_3(6\cos\pi(l-l'))$$
$$+ A_2\left(4\cos\frac{8\pi(l-l')}{6}\right.$$
$$\left.\left. + 8\cos\frac{4\pi(l-l')}{6}\right)\right\}.$$

[9] A. L. Sklar and R. H. Lyddane, J. Chem. Phys. **7**, 374 (1939).

[10] *Handbuch der Physik* (Verlagsbuchhandlung, Julius Springer, Berlin, 1933), Vol. XXIV, p. 643.