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Conformational instability of the lowest triplet state of the benzene nucleus.

I. The unsubstituted molecule

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Experiments on benzene have established that its lowest triplet state ($^3B_{1u}$) is conformationally unstable owing to vibronic coupling with the next higher state ($^3E_{1u}$). This instability was found to be critically dependent on the influence of a crystal field. An analogous vibronic coupling is to be expected in the singlet manifold, but here no direct evidence is available for a conformational instability. The distortion behavior of benzene is of importance for the interpretation of its photophysical and photochemical properties. We have therefore determined the potential-energy surfaces of the $^{1,3}B_{1u}$ and $^{1,3}E_{1u}$ states along the two-dimensional distortion coordinate $S_8(\rho, \varphi)$ using *ab initio* multireference single and double excitation-configuration-interaction calculations. The results show that for both B_{1u} states the hexagonal conformation is unstable and lies 800 cm^{-1} above a wide, virtually cylindrical trough. A calculation of the vibrational spacing in the $^3B_{1u}$ state yields good agreement with the experimentally observed frequency. The calculation of intensities in the absorption and emission spectrum for this state qualitatively agrees with the experiment. An estimate is made of the interaction of the excited molecule with neighboring molecules in a crystal, which indicates that the crystal-field induced energy variations in the trough should be of the order of 10 cm^{-1} . Combination of our calculations with experimental data shows that the vibronic coupling in the B_{1u} states of benzene should not be looked upon as a static coupling in which the molecule is permanently distorted to one conformation but as a dynamic one in which the molecule makes excursions over the entire potential-energy surface.

I. INTRODUCTION

The geometry of benzene in its excited states has been the subject of many experimental and theoretical studies since Moffitt and Liehr showed that vibrational modes of e_{2g} symmetry might couple the lower B_{1u} and B_{2u} singlet and triplet states so strongly to the near E_{1u} state of common molecular-orbital (MO) parentage that the hexagonal conformation is no longer stable.^{1,2} Indeed, low-temperature EPR experiments³ on the metastable triplet state ($^3B_{1u}$) of benzene in a glassy matrix and subsequent EPR (Ref. 4) and electron-nuclear double resonance (Ref. 5) experiments on C_6H_6 in a single crystal of C_6D_6 revealed that in the $^3B_{1u}$ state the electron-spin distribution is nonhexagonal. The structure as proposed from these experiments was an anti-quinoidal one with four short bonds and two long bonds, which is slightly nonplanar and retains only crystallographic site symmetry C_i .

Support for strong vibronic coupling in the lowest triplet state has also been obtained from spectroscopic observations.⁶⁻¹⁶ A key observation was the discovery of an intense doublet 239 and 252 cm^{-1} above the 0-0 transition in the $^3B_{1u} \leftarrow ^1A_{1g}$ absorption spectrum of C_6H_6 by Burland, Castro and Robinson.¹¹ Studies of the Zeeman effect^{13,14} subsequently supported the idea that this doublet in the absorption spectrum should be attributed to the ν_8 (e_{2g}) vibration which has a frequency of 1584 cm^{-1} in the ground state.

Such a large reduction in vibrational frequency in the triplet state, apart from indicating a strong vibronic coupling, would also imply that the potential-energy surface with respect to ν_8 displacements is extremely flat in the excited state compared with the analogous surface for the ground state.

The observations have commonly been interpreted in Moffitt and Liehr's picture of vibronic coupling^{1,2} between two nondegenerate states in which the D_{6h} structure, being a maximum, is surrounded by a trough of lower energy. In first approximation, where only the linear coupling terms between the two states are considered, the trough is cylindrical. Inclusion of second-order terms leads to a trough in which three maxima and three minima are present. If the energy difference between these structures is large enough, a permanent distortion of benzene in the $^3B_{1u}$ state results. If, on the contrary, the energy difference is small with respect to the zero-point vibration of ν_8 , the molecule on average retains its hexagonal symmetry and studies of the $^3B_{1u}$ state of the free molecule will not show a distortion in this state.

The pertinent experimental material stems from studies on solids at low temperature. In the solid a lowering of the symmetry occurs and, owing to the anisotropy of the crystal field or glassy environment, the potential-energy surface of the $^3B_{1u}$ state is modified, thereby favoring certain conformations. In an experiment one may now conclude to a permanent distortion of the molecule in the $^3B_{1u}$ state, even if an analogous experiment on the free molecule would not have

shown this. Indeed, experiments on phosphorescent benzene in various hosts emphasize the importance of the crystal field since the size and even the kind of distortion turn out to be dramatically dependent on the nature of the environment in which benzene is incorporated.¹⁶⁻²¹ A striking example of this behavior is the observation that benzene as a guest in the monoclinic low-temperature stable phase of cyclohexane (phase II) retains an approximately antiquinoidal structure,^{16,19} while in the metastable phase III of cyclohexane the molecule is approximately quinoidal in its lowest triplet state.^{17,19} It might thus well be that the crystal field actually is the decisive factor that determines the average structure of this molecule in its lowest triplet state in experiments on benzene in a solid matrix.

As compared to the triplet state, much less is known about possible distortions in the $^1B_{1u}$ state. In the first instance it was assumed that the effects responsible for the distortion in the $^3B_{1u}$ state should not be qualitatively different for the $^1B_{1u}$ state.^{1,22,23} One- and two-photon excitation experiments performed later on this state seemed to imply that the molecule in the $^1B_{1u}$ state is not distorted.²⁴⁻²⁸

For a long time calculations dealing with the vibronic coupling problem in benzene have been of a semiempirical nature and aimed at obtaining a qualitative interpretation of the spectroscopic and EPR results.^{1,2,29-33} In a series of articles van der Waals *et al.* and van Egmond *et al.*^{22,23,30} considered the vibronic coupling in a formalism analogous to that used in the classical papers on the dynamic Jahn-Teller effect.^{1,34,35} On this basis these authors predicted the remarkable lowering in frequency of ν_8 ,²² while later the influence of higher-order coupling terms in the Hamiltonian,²³ the influence of a crystal field,²³ and the effect of simultaneous coupling through two modes³⁰ were considered. The quantitative results of those studies, though in nice agreement with experimental results, proved extremely dependent on the parameters chosen and should therefore be considered with caution.

Subsequently, Langhoff, Davidson, and Kern³⁶ calculated on an *ab initio* level the energy, fine structure, and hyperfine structure parameters of the $^3B_{1u}$ state for hexagonal benzene and the two distorted conformations that followed from the calculations of Ref. 22. Indeed, it was found that the energy of hexagonal benzene was slightly higher than the energy of the distorted geometries. The calculated fine structure and hyperfine structure parameters of the hexagonal and distorted geometries, on the contrary, indicated that the hexagonal structure with slightly longer bond lengths than in the ground state resulted in values closer to the experimental values than those which resulted from the two distorted geometries considered. Their conclusion was that the conformation observed experimentally is on average nearly hexagonal with only a slight elongation.

Recently, and simultaneous with our present studies, Osamura made a complete active space multiconfiguration self-consistent-field (CAS-MCSCF) study of the $^3B_{1u}$ state in which the extrema along a cut through the ν_8 potential-energy surface were searched for.³⁷ He found the D_{6h} geometry to be unstable and calculated the quinoidal conformation to be 493 cm^{-1} lower in energy while the antiquinoidal min-

imum was lowered by 366 cm^{-1} . In his study only π electrons were correlated, and when considering the small energy differences, it might well be that σ - π and σ - σ correlations play a role comparable to these energy differences.

In order to obtain a clear picture of the distortion in the lowest triplet state and to find out to what extent this distortion might be different in the $^1B_{1u}$ state, we have performed large configuration-interaction (CI) calculations, including σ - σ and σ - π correlation, to determine the potential-energy surfaces of both the $^3B_{1u}$ and $^1B_{1u}$ states along Wilson's symmetry coordinate $S_8(\rho, \varphi)$,³⁸ thought to be dominant in the vibronic coupling. For comparison, we also calculated the potential-energy surface of the $^3E_{1u}$ and $^1E_{1u}$ states to which the states under consideration are coupled, together with the corresponding surface of the ground state. In a recent communication³⁹ we gave a brief account of the calculations on the $^3B_{1u}$ state. Here we wish to examine in greater detail the distortion of the B_{1u} states and to consider the implications of our calculations for the interpretation of the experimental results.

Even though these potential-energy surfaces enlighten us about the vibronic coupling in the B_{1u} states, the static picture does not enable us to make any comparisons with experimental results. To explain these results we have solved the Schrödinger equation for nuclear motion in the two-dimensional well defined by the calculated potential-energy surface and obtained the vibrational energy levels and wave functions. It will be shown that the main features of the spectroscopic observations are nicely recovered in this way.

Strictly speaking the results mentioned above apply for the free molecule only. For observations in the solid phase we have to take the crystal field into account, certainly when considering that the distortion of benzene is so dependent on the environment.¹⁶⁻²¹ By combining our potential-energy surface of the $^3B_{1u}$ state with an additional calculation on the interaction of a benzene molecule with its neighbors in the crystal, we shall make it plausible that it is the crystal field which determines the distortion of benzene in its lowest triplet state. This distortion should, however, not be considered as a static one, but as a distortion that results from an averaging over the complete potential-energy surface, both in the radial as well as in the tangential coordinate.

II. COMPUTATION OF THE POTENTIAL-ENERGY SURFACES

A. Geometry and distortion coordinate

In our calculations we assume that the vibronic coupling between the B_{1u} and E_{1u} states occurs via the e_{2g} symmetry mode S_8 . Although for the excited states considered the normal coordinates are not known it is generally assumed that of the four symmetry modes of e_{2g} symmetry the carbon-carbon stretching and skeletal bending modes S_8 and S_6 should be the most important ones in vibronic coupling. Using arguments based on symmetry, Moffitt⁴⁰ pointed out that the striking difference in vibronic structure between the $^3B_{1u} \leftarrow ^1A_{1g}$ phosphorescence and $^1B_{2u} \leftarrow ^1A_{1g}$ fluorescence spectra arises because coupling between B_{1u} and E_{1u} states is effected predominantly by the stretching

mode S_8 , while that between B_{2u} and E_{1u} states is effected by the bending mode S_6 .

The potential-energy surfaces were calculated along the symmetry coordinate $S_8(\rho, \varphi)$ expressed in polar coordinates as^{1,2,41}

$$\begin{aligned} Q_{8a} &= \rho \cos \varphi, \\ Q_{8b} &= \rho \sin \varphi. \end{aligned} \quad (1)$$

Even if in reality some scrambling of the four e_{2g} symmetry modes might occur in the B_{1u} states, distortion along S_8 should be able to explain the major effects.⁴⁰ The corresponding variations in bond lengths are depicted in Fig. 3 for three values of the angle φ . For $\varphi = 0^\circ$, 120° , and 240° the so-called quinoidal conformations (four long bonds, two short bonds) are obtained, while for $\varphi = 60^\circ$, 180° , and 300° the antiquinoidal conformations (four short bonds, two long bonds) are generated. In a fixed axes frame the symmetry of the molecule is lowered from D_{6h} to D_{2h} for $\varphi = 0^\circ$ and 180° , but for $\varphi = 90^\circ$ only C_{2h} symmetry is retained. In the rest of this article calculations will therefore be classified as D_{2h} or C_{2h} calculations.

When the molecule is distorted to any of these conformations, the E_{1u} state is no longer degenerate, but splits into two components. Only the component that belongs to the same irreducible representation of the groups D_{2h} or C_{2h} as the B_{1u} state will be considered here.

For the hexagonal conformation of benzene a geometry was chosen with an experimental C–H distance of 1.085 Å and a C–C distance optimized to give the lowest energy of the $^3B_{1u}$ state in D_{6h} symmetry (1.440 Å). As expected this distance is somewhat larger than the equilibrium distance in the ground state (1.395 Å). In deforming the molecule, the H atoms move rigidly with their corresponding C atoms.

B. Atomic-orbital basis set

For the carbon atoms the (9s5p) Cartesian Gaussian basis set contracted to [4s2p] according to Fischer-Hjalmar (basis B') was used.⁴² This set had been optimized for ethylene and proved successful in calculations on the ground state of benzene. Because the states considered here are likely to be more diffuse in character than the ground state, the outermost p function was contracted in a slightly different way. For the hydrogen atoms the standard (5s) set contracted to [2s] by Dunning⁴³ was employed with orbital exponents scaled by a factor of 1.44 (1.2²). The effects of the latter scaling can be seen in Ref. 44, where basis-set effects were investigated in Hartree–Fock studies on the ground state of benzene; a conclusion drawn from this study is that, though the optimized C–H bond lengths are somewhat smaller than without scaling, the final energy is lower. Polarization functions, i.e., d -type Gaussians on C and p -type Gaussians on H, were not included. Their inclusion would have led to a nearly five fold increase in computer time, and the influence of such functions on the relative energies in the neighborhood of the equilibrium geometry is rather small, even though they contribute noticeably to the correlation energy.³⁷

With this atomic-orbital (AO) basis set selected for calculations on the triplet state we obtain an SCF energy for the

$^1A_{1g}$ ground state of -230.6302 H using the conformation given by Stevens *et al.*⁴⁵ ($R_{cc} = 1.395$ Å; $R_{CH} = 1.085$ Å). This energy is slightly higher than the values obtained by Hay and Shavitt⁴⁶ using the regular contraction scheme of the (9s5p) set of Dunning (-230.6410 H), by Ermler and Kern⁴⁷ who used the same basis set but with different scaling factors for the σ and π components of the $2p$ functions (-230.6457 H), and by Langhoff, Davidson, and Kern³⁶ who used the same Dunning basis for the carbons but a [3s] basis for the hydrogen atoms (-230.6437 H). However, owing to our contraction scheme the basis set we use is slightly more diffuse than the basis sets of the above authors, and the optimal C–C bond length associated with our basis for the ground state is likely to be different from that of the Dunning basis. It is important, however, that with our basis set the CI expansion turns out to converge more rapidly and a larger part of the correlation energy is recovered in comparison with the Dunning basis set for both the ground state as well as the $^3B_{1u}$ state.

C. CI procedure and MO basis

The CI calculations used the CRAY-XMP version of the Wuppertal–Bonn multireference, single- and double-excitation configuration interaction (MRDCI) method with configuration selection and extrapolation of the energy to the complete generated MRDCI space by a perturbation method.⁴⁸ An estimate of the energy corresponding to the full-CI space within the AO basis was made according to the formula given in Ref. 49. In the MRDCI method a set of configurations with the proper symmetry is generated from the single and double excitations from a given set of reference configurations. Subsequently they are selected on an energy lowering criterium. In the calculations on benzene the MO set of 72 functions was truncated to 54 functions by elimination of the 18 σ -type orbitals of highest orbital energy. Furthermore, the lower 11 σ -type orbitals were kept doubly occupied resulting in a CI in which 20 electrons are correlated.

The $^{1,3}B_{1u}$ and $^{1,3}E_{1u}$ states of benzene are in first approximation two-configuration states with equal weights for both configurations in D_{6h} symmetry. In Fig. 1 these configurations are depicted and named according to their dominance in the CI function of quinoidal (Q) or antiquinoidal (A) structures.

The molecular orbitals used in the CI calculations are the orbitals which result from an SCF calculation for the $^5A_{1g}$ quintet state: $\cdots (1a_{2u})^2 (1e_{1g})^2 (e_{2u})^2$. In this way the σ core relaxation, which was shown to be important by Matos, Roos, and Malmqvist⁵⁰ in a recent CASSCF-CCI (contracted configuration interaction) study, is anticipated. The use of the $^5A_{1g}$ orbitals furthermore allows for an unambiguous treatment of conformations with lower symmetry than D_{6h} , where the occupation numbers of the components of the $1e_{1g}$ and $1e_{2u}$ orbitals are no longer 1.5 and 0.5, respectively. Problems associated with a single-determinant SCF calculation for a two-configuration state are in this way circumvented.

The need to use open-shell SCF MOs was underlined by CI calculations on the lowest triplet state which we per-

FIG. 1. Orbital scheme of the six important π electron MOs with their symmetries in the D_{6h} point group. The dashed lines indicate nodal plane(s) present in the MO. The two configurations are labeled according to their dominance in the wave functions of the lowest triplet state for anti-quinoidal (*A*) and quinoidal (*Q*) conformations.

formed with the SCF orbitals of the ground state. The use of these orbitals led to a slower convergence of the CI expansion and required the inclusion of a very large and carefully selected and balanced reference set to generate smooth potential-energy surfaces for the excited states considered here. Another approach we tried was the use of the natural orbitals (NOs) for the state under consideration,⁵¹ generated from the CI expansion with $^1A_{1g}$ MOs. Though in that case the convergence proved somewhat faster, the selection of reference configurations still required great care. Separation of the π - π from the σ - π and σ - σ correlations showed that the main cause for this behavior was indeed the absence of σ -core relaxation in the $^1A_{1g}$ orbitals.

For the calculations of the $^3B_{1u}$ and $^3E_{1u}$ states a set of reference configurations was used that consisted of the 15 configurations with a coefficient having an absolute value larger than 0.05 in either the $^3B_{1u}$ or $^3E_{1u}$ state. Selection on the lower two roots of the zeroth-order CI expansion with an energy threshold of 15 μ H resulted in CI matrices which varied in size between 3000 and 8000 configurations out of 454 024, depending on the geometry considered.

The $^1B_{1u}$ and $^1E_{1u}$ states have been studied using a set of those 19 reference configurations that had a coefficient with an absolute value larger than 0.05 in either the $^1B_{1u}$ or $^1E_{1u}$ CI expansion. For the $^1B_{1u}$ and $^1E_{1u}$ states only the D_{2h} distortions have been considered.

Finally, in order to compare the calculated potential-energy surfaces of the excited states with that of the ground state, a calculation along the D_{2h} distortion coordinate was made for the $^1A_{1g}$ state. The C-C bond length, however, was not the one optimal for the ground state but the optimized one of the lowest triplet state. The MOs used in the CI calculations on this state are the SCF orbitals of the ground state. In this case a set of six reference configurations was needed

to meet the same selection criterion for the reference configurations as for the other states.

III. RESULTS

In Figs. 2 and 3 the calculated potential-energy surfaces of the ground state and the $^3B_{1u}$ and $^3E_{1u}$ states are shown for distortions along the $S_8(\rho, \varphi)$ coordinate. Table I gives some characteristics of the calculations on these states for hexagonal benzene with $R_{CC} = 1.440$ Å.

For the ground state (Fig. 2) the hexagonal geometry according to our calculations is not exactly that of lowest energy. This can be understood since the bond length used in the calculations is the somewhat longer bond length optimal for the $^3B_{1u}$ state. Furthermore, it is clear that the potential is only slightly anharmonic.

The most striking feature of the $^3B_{1u}$ surface (Fig. 3) is its flatness over a wide area compared with the potential-energy surface of the ground state. The hexagonal conformation is no longer stable but is about 800 cm^{-1} higher in energy than a region of minimal energy which occurs at a ρ value of 0.0185 Å. The variation with φ in this region is smaller than the error of ± 100 cm^{-1} in the relative energies estimated from a least-squares fit of a polynomial in ρ to the points of Fig. 3, plus a set of similar points resulting from a calculation based on 11 configurations. On the other hand, the surface of the component of the $^3E_{1u}$ state which interacts with $^3B_{1u}$ state resembles the ground-state surface, albeit the energy rises much faster as a function of ρ .

Qualitatively the potential-energy surface for the $^3B_{1u}$ state agrees with that calculated in the past by one of us using semiempirical methods.²² The size of the distortion is almost equal in the two calculations but the energy differences accompanying the distortion are considerably smaller in the present calculation. With respect to the size of the distortion our results agree also with the geometry optimization of Padma Malar and Jug,³³ who used the semiempirical SINDO (symmetrically orthogonalized intermediate neglect of differential overlap) 1 approach. They found a quinoidal form with a value of ρ similar to ours.

Recently, Osamura reported a CAS-MCSCF geometry optimization study of the $^3B_{1u}$ state, correlating the π electrons only.³⁷ The maximum and minimum reported along a cut of the potential-energy surface along the ν_8 coordinate

FIG. 2. Potential-energy surface for the $^1A_{1g}$ state along the $S_8(\rho, \varphi)$ symmetry coordinate. The zero of energy corresponds to the energy of the $^1A_{1g}$ state in the hexagonal conformation and $\varphi = 0^\circ$ and $\varphi = 180^\circ$ correspond to quinoidal and anti-quinoidal conformations, respectively.

FIG. 3. Potential-energy surfaces along the $S_8(\rho, \varphi)$ symmetry coordinate for the ${}^3B_{1u}$ state (solid line) and that component of the ${}^3E_{1u}$ state (dashed line) to which the ${}^3B_{1u}$ state is vibronically coupled. The zero of energy is equal to the energy of the ${}^3B_{1u}$ state in the hexagonal conformation. The bars represent estimates of the possible errors in the extrapolation process of the MRDCI method (Ref. 49).

indicate a value of $0.016 \text{ \AA}$ for ρ , consistent with our conclusion. The stabilization energy of the distorted quinoidal and antiquinoidal geometries of minimal energy, however, is only about half of that found by us. Moreover, our calculations suggest that the energy difference between these two geometries is even smaller than the energy difference of 127 cm^{-1} predicted by Osamura.

Though it is now clear that in a static picture the hexagonal conformation is unstable, for the dynamic behavior it is important to know how large the energy variations are in the trough. The size of these variations will determine if the lower ν_8 vibrational levels should be considered as free or hindered pseudorotor levels, and thereby, indirectly, what influence a crystal field can have on the distortion. The calculations represented in Fig. 3. show that the dependence of the energy on φ at the bottom of the well is small and, what is particularly relevant for comparison with experiment, also substantially smaller than the vibrational quantum for nuclear motion in the potential well of Fig. 3. We have repeated our calculations with various smaller sets of reference configurations and found that the energy differences are negligibly influenced by the choice of the reference set.

We also made a calculation in which only the π electrons are correlated. This calculation with a reference set of 18 configurations, 6 π electrons, and 12 π orbitals, generates 1668 configurations of the proper symmetry which were all used for the CI expansion. The energy differences between the hexagonal maximum and the quinoidal and antiquinoidal minima are 420 and 250 cm^{-1} , respectively, in reasonable agreement with the results of Osamura. As we saw, both differences are equal to 800 cm^{-1} in the more extensive CI calculations described above, so apparently, correlation with the σ electrons is important. Even if the σ reorganization is relatively small for the lowest triplet state of benzene, as

TABLE I. Characteristics of the CI calculations of the ground state and the lower excited singlet and triplet states of benzene for the hexagonal conformation ($1 \text{ H} = 219\,474.63 \text{ cm}^{-1}$).

	${}^1A_{1g}$	${}^1B_{1u}$	${}^1E_{1u}$
No. reference configurations		6	19
No. generated configurations		138 224	307 890
Threshold T (μH)		15	15
No. selected configurations at T		2590	4321
E_{rc}^a (H)		-230.6782	-230.3661
$E(T)^b$ (H)		-230.8748	-230.5529
$E(T=0)^c$ (H)		-230.9018	-230.6124
Extrapolation uncertainty (H)		0.0014	0.0030
$E(T=0) + E_{\text{Dav}}^d$ (H)		-230.9207	-230.6346
$\sum_{i=1}^{\text{ref}} c_i^2$		0.9233	0.9098
		${}^3B_{1u}$	${}^3E_{1u}$
No. reference configurations		15	15
No. generated configurations		454 024	454 024
Threshold T (μH)		15	15
No. selected configurations at T		3817	3817
E_{rc}^a (H)		-230.5383	-230.4933
$E(T)^b$ (H)		-230.6674	-230.6267
$E(T=0)^c$ (H)		-230.7590	-230.7233
Extrapolation uncertainty (H)		0.0046	0.0048
$E(T=0) + E_{\text{Dav}}^d$ (H)		-230.7740	-230.7398
$\sum_{i=1}^{\text{ref}} c_i^2$		0.9320	0.9283

^a Energy after CI with only the reference configurations.

^b Energy at threshold T .

^c Energy extrapolated to $T=0$.

^d Energy $E(T=0)$ corrected with the Davidson correction (Ref. 49).

^e Sum of squared contributions of the reference configurations in the final CI expansion.

concluded from a recent SACCI (symmetry-adapted cluster configuration interaction) calculation of transition energies,⁵² the energy differences involved in the distortion of benzene in the ${}^3B_{1u}$ state are so small that this correlation still plays an important role. It not only adds to the stabilization of the quinoidal and antiquinoidal geometries, and also compensates for the preference in the π electron picture for the quinoidal geometries.

In Fig. 4 the potential-energy surface for the ${}^1B_{1u}$ and ${}^1E_{1u}$ states along $S_8(\rho, \varphi)$ (D_{2h}) are shown. In Table I the characteristics of the calculation for these states in the hexagonal geometry are given. Comparison of the surfaces of the ${}^1B_{1u}$ and ${}^1E_{1u}$ states with the surfaces of the ${}^3B_{1u}$ and ${}^3E_{1u}$ states shows no significant differences: the region of minimal energy in the ${}^1B_{1u}$ state occurs for the same value of ρ , and also the stabilization energy is the same as for the ${}^3B_{1u}$ state. In the description of the singlet states we deal with states that have been found to possess considerable ionic character.^{50,52} Consequently, a proper description of these states would require larger basis sets with diffuse orbitals and larger CI calculations to describe the intra-atomic correlation effects. Nevertheless, the relative energy differences which occur on distortion of the molecule should still be reliable, but the excitation energy will be more in error than for the corresponding triplet states.

Unfortunately, the spectroscopic data for the ${}^1B_{1u}$ state²⁴⁻²⁸ are scantier and less conclusive than for the ${}^3B_{1u}$ state. Though the position of this state is well determined, the interpretation of its poorly resolved vibronic structure seems to be uncertain. Still, the favored interpretation nowadays is one in which the molecule retains its hexagonal shape and the frequency of ν_8 does not change as much as in the

lowest triplet state. This was supported by the geometry optimization in the SINDO1 calculation of Padma Malar and Jug,³³ from which it was concluded that merely an increase in bond lengths occurs in the ${}^1B_{1u}$ state.

Our calculations, on the contrary, support the original proposition put forward by Liehr² and later by van der Waals, Berghuis, and de Groot,²² namely, that the effects in the singlet and triplet manifolds are not qualitatively different. This is also what one would expect considering the Herzberg-Teller expansion of the wave function of the B_{1u} state:

$$B_{1u} = B_{1u}^0 + \sum_{j \neq B_{1u}^0} \sum_v \langle B_{1u}^0 | \left(\frac{\partial \mathcal{H}_e}{\partial Q_v} \right)_{Q_v=0} | \Psi_j^0 \rangle \times (E_{B_{1u}^0}^0 - E_j^0)^{-1} Q_v \Psi_j^0 + \dots \quad (2)$$

As shown before, the major contribution arises from coupling to the E_{1u} state via e_{2g} vibrations and notably via ν_8 .¹ In first approximation both the singlet and triplet B_{1u} and E_{1u} states are constructed from the same spatial orbital configurations, and since $(\partial \mathcal{H}_e / \partial Q_v)_{Q_v=0}$ is independent of the spin function, the coupling of ${}^{1,3}E_{1u}$ to ${}^{1,3}B_{1u}$ will in first order only depend on the energy difference between the B_{1u} and E_{1u} states. Experimentally, it has been determined that this difference is nearly equal for the singlet and triplet manifolds (0.7 and 0.8 eV, respectively);⁵³⁻⁵⁶ numbers which are confirmed by our calculations which give 0.9 and 1.0 eV for the singlets and the triplets, respectively.

Our calculations show that both the ${}^3B_{1u}$ and ${}^1B_{1u}$ states are unstable with respect to an S_8 distortion. However, one would like to get an intuitive picture of the changes occurring in the wave functions or charge densities of those states. One of the properties which might give insight is the populations on the atoms and in the bonds as functions of the distortion. Though it is known that the absolute numbers obtained from a population analysis are strongly dependent on the basis set, trends should still be clear.

In Fig. 5 the population differences between the ${}^{1,3}B_{1u}$ states and the ${}^1A_{1g}$ state have been drawn for the D_{2h} distortion, both for the populations on the carbon atoms and in the C-C bonds. In the hexagonal symmetry the characteristics of the ${}^{1,3}B_{1u}$ states are well demonstrated. Though the total population on the atoms remains nearly the same on excitation, the distribution of the electrons is altered dramatically: the atoms obtain a larger fraction of the population while the population in the bonds is lowered. This behavior reflects the fact that the excited states are no longer strictly aromatic, since effectively one electron has been excited from a bonding orbital to an antibonding orbital.

In the B_{1u} states localization occurs because of the excitation to an antibonding orbital. For quinoidal conformations the effects of the antibonding character are partially compensated by the localization of an electron on C_1 and the formation of a double bond between C_2 and C_3 , while in the antiquinoidal conformations the localization occurs by the formation of two allyl fragments and a weakening of the π bond between C_2 and C_3 . Consequently, one might say that in the B_{1u} states the antibonding effect of the excited electron tends to be compensated by a partial localization upon dis-

FIG. 4. Potential-energy surfaces along the $S_8(\rho, \varphi)$ symmetry coordinate for the ${}^1B_{1u}$ state (solid line) and that component of the ${}^1E_{1u}$ state (dashed line) to which the ${}^1B_{1u}$ state is vibronically coupled. The zero of energy corresponds to the energy of the ${}^1B_{1u}$ state in the hexagonal conformation.

FIG. 5. Variation with the $S_n(\rho, \varphi)$ symmetry coordinate of the populations on carbon atoms and in bonds between the carbon atoms. In the figure the difference of a certain population with the corresponding population in the ground state is plotted. In (a) the populations in the ${}^3B_{1u}$ state are given; in (b) the populations in the ${}^1B_{1u}$ state.

tortion. It is also recognized that in the ${}^1B_{1u}$ state somewhat more localization occurs than in the ${}^3B_{1u}$ state, in line with the ionic character of the former state.

In the ground state only very small changes occur (less than 0.02 for $\rho = 0.03$ Å) upon distortion, showing that the delocalization of the π electrons is not destroyed at all for the geometries considered here.

IV. COMPARISON WITH EXPERIMENT

A. The vibronic levels

The potential-energy surfaces for the lower electronic states of benzene which follow from our calculation, by their nature, represent an intermediate result that cannot be compared with experiment. In order to find out if these potentials are realistic one has to solve the Schrödinger equation including nuclear motion. The experimental information that can be used to test our results refers almost entirely to the lowest triplet state. We, therefore, merely consider the vibronic solutions for the ${}^3B_{1u}$ potential. Since this state is orbitally nondegenerate, we adopt the Born–Oppenheimer approximation and remain within the two-dimensional representation adopted thus far. The Schrödinger equation for the nuclear motion in the potential $V(\rho, \varphi)$ can then be written as⁵⁷

$$\left[-\frac{1}{2\mu} \left(\frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \varphi^2} \right) + V(\rho, \varphi) \right] \chi_{v,l} = E_{v,l} \chi_{v,l}. \quad (3)$$

The labeling of the eigenfunctions is that appropriate for a two-dimensional isotropic harmonic oscillator [$V(\rho, \varphi) = V(\rho) = \rho^2$] where l and v are good quantum numbers. The number l represents the angular momentum associated with the degenerate vibration, which can take the values $-v, -v+2, \dots, v-2, v$, while v measures the energy, $E_{v,l} = (v+1)h\nu_8$. Alternatively, v can be interpreted as a quantum number that counts the total number of nodes, i.e., twice the number of radial nodes in $\chi_{v,l}$ plus $|l|$.

In our case of the lowest triplet state of benzene we have to deal with a two-dimensional oscillator in a highly anharmonic potential which, moreover, may vary with φ . We have first approximated the potential that results from a static calculation by a function of the form

$$V(\rho, \varphi) = \sum_{i=0}^{i_{\max}} \rho^i (b_{i,0} + b_{i,3} \cos(3\varphi)). \quad (4)$$

Then we solved Eq. (3) using a variational approach⁵⁸ in which the eigenfunctions $\chi_{v,l}$ are expanded as

$$\chi_{v,l}(\rho, \varphi) = \sum_{n=0}^{n_{\max}} \rho^n e^{-\alpha \rho^2} \{ C_{v,l,n,l} \cos(l\varphi) + C_{v,l,n,(l-3)} \cos[(l-3)\varphi] + C_{v,l,n,(l+3)} \cos[(l+3)\varphi] \}. \quad (5)$$

In the calculations to be described $n_{\max}$ was set equal to 30, which is equivalent to restricting the radial function space to that of the first 30 Hermite polynomials.

We will consider in the following two kinds of potential-energy surfaces. In the first the potential is taken independent of φ ($b_{i,3} = 0$). In that case $C_{v,l,n,(l-3)}$ and $C_{v,l,n,(l+3)}$ in Eq. (5) are zero and l remains a good quantum number. In the second case a φ -dependent potential is taken ($b_{i,3} \neq 0$). For such a potential l is not a good quantum number anymore because a mixing occurs between functions that differ in their l value by ± 3 . Our calculations show that only a slight mixing occurs, and consequently we will continue to label the vibrational eigenfunctions with l . Although for an anharmonic potential-energy surface v is not a good quantum number we can still label the vibrational eigenfunctions with v if we define v in terms of the total number of nodes as described above.

According to our calculations the potential-energy surface for the lowest triplet state is virtually φ -independent, and we therefore first solved Eq. (3) for the two φ -independent potentials shown in Figs. 6(a) and 6(b). The potential of Fig. 6(a) represents a fit with the aid of Eq. (4) to the results of our calculations of Sec. III A for the structures of C_{2h} symmetry. The six lower vibrational levels calculated for this potential are listed in Table II and shown in Fig. 7. The separation between the first two levels is 220 cm^{-1} , which compares surprisingly well with the energy difference between the zero-point level and a doublet at 239 and 252 cm^{-1} observed in experiments on C_6H_6 in a C_6D_6 host crystal.¹¹ The splitting into a doublet is attributed to the anisot-

FIG. 6. Potential-energy surfaces of the ${}^3B_{1u}$ state used in the calculation of the vibronic levels and wave functions. (a) ϕ -independent potential with a stabilization energy (800 cm^{-1}) in the energy minima equal to that obtained in the calculations of Sec. III for the structures of C_{2h} symmetry. (b) Same as (a) but the stabilization energy is now 430 cm^{-1} , the mean value of the minima of Ref. 37. (c) ϕ -dependent potential; the bottom of the trough is still cylindrical with a depth of 800 cm^{-1} but the walls of the potential-energy surface vary with ϕ in accordance with the results of the calculations of Sec. III for the quinoidal and antiquinoidal conformations of large ρ . (d) ϕ -dependent potential; the bottom of the trough varies in depth from 493 cm^{-1} (quinoidal conformations) to 366 cm^{-1} (antiquinoidal conformations) in accordance with Ref. 37, while the walls at large ρ are those of (c).

ropy of the crystal field which removes the degeneracy of the ($v = 1; l = \pm 1$) levels. This degenerate character of the second level is nicely borne out by our calculations since it is doubly degenerate in l . As we go higher up in vibrational energy it is seen that the order of the levels is such that of the levels associated with a certain v , the one with the highest

TABLE II. Energies in cm^{-1} of the six lower vibrational levels of $S_0(\rho, \phi)$ in the ${}^3B_{1u}$ state. Energy is defined with respect to the energy of the lowest triplet state for a hexagonal geometry. (a), (b), (c), and (d) refer to the potential-energy surfaces of Fig. 6.

v, l	(a)	(b)	(c)	(d)
0; 0	-335	-111	-339	-125
1; ± 1	-115	126	-114	110
2; ± 2	258	488	259	484
2; 0	591	721	591	706
3; ± 3	726	931	729	925
3; ± 1	1066	1200	1066	1189

FIG. 7. Energy levels of the six lower vibronic levels in the potential-energy surface of the ${}^3B_{1u}$ state. The quantum numbers v and l are defined in Sec. IV A. The potential used for the calculation is that of Fig. 6(a).

angular momentum l is lowest in energy, in accordance with earlier calculations.^{22,23}

In Fig. 8 we show the form of the radial part of the eigenfunctions $\chi_{v,l}$ for the six lower vibronic levels. The ($v = 0; l = 0$) level is of particular interest since in a low-temperature experiment on the molecule in its lowest triplet state it will be the properties of this level which determine the result. The wave function of this level by no means is confined to the trough of minimal energy but extends over the complete surface. For the higher levels the vibrational eigenfunctions approach those of a true two-dimensional harmonic oscillator, though the degeneracy is distinctly removed by the anharmonicity of the potential surface.

Next we consider the cylindrical potential of Fig. 6(b), in which the depth of the trough has been decreased to the mean value (430 cm^{-1}) of the stabilization energy for the antiquinoidal and quinoidal conformations of minimal energy found by Osamura (366 and 493 cm^{-1} , respectively).³⁷ A comparison of the vibrational energies given in columns (a) and (b) of Table II reveals that the splitting between the lower levels is only changed by 8% (Table III) even though the stabilization energy is decreased by 50% on going from Fig. 6(a) to 6(b). This, together with the two examples to be given in the next paragraph, proves that the main cause for the impressive energy lowering in frequency of ν_8 in the ${}^3B_{1u}$ state must in the first instance not be sought in the value of the stabilization energy but rather in the large width and relative flatness of the potential well.

In Figs. 6(c) and 6(d) we finally consider two potential

FIG. 8. Shape of the vibronic wave function for the six lower vibronic levels in the potential of Fig. 6(a).

surfaces that are φ dependent. Figure 6(c) represents a fit of the calculations of Sec. III A to Eq. (4); while the potential near the bottom of the trough ($\rho \approx 0.018$ Å) is φ independent, the walls of the potential-energy surface vary with φ in accordance with the results of our calculations for the quinoidal and antiquinoidal conformations of large ρ . In Fig. 6(d) the energy differences in the trough for $\varphi = 0^\circ$ and 180° are as calculated by Osamura while the walls are the same as in Fig. 6(c). The potential energy surfaces of Figs. 6(c) and 6(d) were fitted according to Eq. (4) with $b_{i,3} \neq 0$. The vibrational energies in Table II show that for Fig. 6(c), where only an anharmonicity in the walls is present, the vibrational levels are nearly identical to those of the cylindrical potential [Fig. 6(a)]. For case Fig. 6(d), however, the lower levels are shifted in energy by some 10% relative to Fig. 6(b). The energy difference between the two lower levels (Table III), on the contrary, is not affected, even with a difference of 127 cm^{-1} between the minima in the trough. This result once again stresses that the frequency of ν_8 is primarily deter-

mined by the flatness of the surface and not by small energy differences in the trough.

In the past it has been assumed that the lower vibrational levels of the $^3B_{1u}$ state could be considered as the energy levels of a free or hindered rigid pseudorotor, which would make it possible to calculate the vibrational energy levels from the value of ρ at the minimum of the trough.^{22,37} Our calculations show that this certainly is not the case. The $S_8(\rho, \varphi)$ vibration in the $^3B_{1u}$ state should be looked upon as a vibrator, in which the radial and tangential motions are strongly coupled. As a consequence, a calculation of the second derivative of the energy at the conformations of minimal energy is inadequate for predicting frequencies³⁷ since the vibrational wave functions extend over the complete, highly anharmonic potential-energy surface.

B. Radiative properties

In this section we examine how far our preceding results are compatible with some of the remarkable features in the intensity distribution in the emission and absorption spectra of benzene. Although the phosphorescence spectrum may acquire intensity through vibronic coupling of the $^3B_{1u}$ state to $^3E_{1u}$ via all four modes of e_{2g} symmetry, the theoretical considerations of Moffitt and Liehr^{1,2} have made it clear why the mode S_8 , which is dominant in the phosphorescence spectrum, is particularly effective. The 8_1^0 band is by far the strongest band in the phosphorescence of benzene and the 8_3^0 band also carries a substantial intensity; according to Nienman¹⁰ their reduced intensity ratio is $I(8_3^0)/I(8_1^0) = 0.16$. We have calculated this ratio using the ($v = 0; l = 0$) vibrational wave function obtained for the $^3B_{1u}$ state and the ($v = 1; l = \pm 1$) and ($v = 3; l = \pm 1$) wave functions of the ground state, which we generated on the basis of Eq. (3) to (5) using the potential-energy surface of the ground state (see Fig. 2). On the basis of Franck-Condon factors we obtain a value $I(8_3^0)/I(8_1^0) = 0.25$, which agrees qualitatively with the experimental value. In Table III we compare this result with similar results obtained with the vibrational wave functions of the surfaces of Figs. 6(b), 6(c), and 6(d). It appears that the anharmonicity of the walls does not affect this ratio but that a reduction of the stabilization energy lowers its value significantly.

Another intensity ratio of interest is the ratio

TABLE III. Calculated and experimental values of the first vibronic spacing and the relative intensities of vibronic bands in the triplet $\leftrightarrow$ singlet spectra of benzene. The columns (a), (b), (c), and (d) refer to the potential-energy surfaces of Fig. 6.

	(a)	(b)	(c)	(d)	Exp.
$E(1; \pm 1) - E(0; 0) \text{ (cm}^{-1}\text{)}$	220	237	225	235	245
$I(8_3^0)/I(8_1^0)^a$	0.25	0.20	0.25	0.19	0.16
$I(8_3^0)/I(8_3^0)^a$	3.0	3.2	3.0	3.2	≈ 3
$I(8_3^0)/I(8_1^0)^b$	0.50	0.39			0.16
$I(8_1^0)/I(8_3^0)^b$	3.1	3.2			≈ 3

^a Based on Franck-Condon factors.

^b Based on Eq. (10).

$I(8_1^0)/I(8_0^1)$. From absorption experiments the ratio $I_{(0-0)}/I(8_0^1)$ is estimated to be about 0.05,¹¹ while from the phosphorescence spectrum $I_{(0-0)}/I(8_0^1)$ was determined as 0.017 ± 0.002 .³⁰ We calculate $I(8_1^0)/I(8_0^1) = 3.0$, which is compatible with the experimental estimate. Table III shows that this ratio is practically independent of the potential chosen.

Although these ratios agree qualitatively with the experimental results, a quantitative discrepancy in $I(8_1^0)/I(8_0^1)$ remains. The main cause, probably, is that ν_8 in the ground state actually is of a different composition of e_{2g} symmetry coordinates than in the $^3B_{1u}$ state. This appears to be supported by force field calculations⁵⁹⁻⁶² which show a considerable contribution of S_6 and S_9 to ν_8 in the ground state, but even more by the measured absorption and phosphorescence spectra of benzene. In these spectra bands involving vibrations of e_{2g} symmetry other than ν_8 show considerable activity, especially the ν_9 vibration.^{10,16} The ν_9 vibration, however, is not expected to be active in the coupling between the B_{1u} and the E_{1u} states,⁴⁰ nor is it to be expected that it indirectly affects the transition probability from the lowest triplet state to the ground state via a coupling in the singlet manifold (the latter possibility has been invoked to explain the activity of the ν_6 vibration).¹⁶ Consequently, it seems plausible that ν_9 derives its activity from a substantial overlap of ν_8 in the lowest triplet state with ν_9 in the ground state.

We have also investigated a more subtle reason that could affect the comparison between the calculated and experimental intensity ratios: is it, in fact, correct to use the Franck-Condon factors in the present situation without taking into account the route via which the $^3B_{1u}$ state obtains its radiative character?

In a crude Born-Oppenheimer (CBO) basis the spatial part of the wave function of the vibronically coupled B_{1u} state may be written as

$$\Psi(q; \rho, \varphi) = \mu(\rho) \Psi_{B_{1u}}^0 + \lambda(\rho) \frac{1}{\sqrt{2}} (\Psi_{E_{1u}}^0 e^{i\varphi} + \Psi_{E_{1u}}^0 e^{-i\varphi}) + \dots, \quad (6)$$

in which q represents the electronic coordinates and Ψ_Γ^0 ($\Gamma = B_{1u}, E_{1u}^\pm$) are the wave functions in D_{6h} symmetry. This equation is consistent with the rotational symmetry since, if $R = C_{2\pi/6}$ and $\omega = e^{2\pi i/6}$, then $R\Psi_{B_{1u}}^0 = \omega^3\Psi_{B_{1u}}^0 = -\Psi_{B_{1u}}^0$ and $R\Psi_{E_{1u}^\pm}^0 e^{i\varphi} = \omega\Psi_{E_{1u}^\pm}^0 \omega^2 e^{i\varphi} = -\Psi_{E_{1u}^\pm}^0 e^{i\varphi}$ (cf. Ref. 22). We now have to take into account the experimental observation that the emission from the $^3B_{1u}$ state stems from the $|x\rangle$ and $|y\rangle$ spin components of the triplet manifold in zero field because this emission, as in other aromatic hydrocarbons, is polarized out of plane.¹⁶ From symmetry considerations it then follows that the radiative character admixed to the $^3E_{1u}$ state comes from $^1A_{2u} \sigma\pi^*$ and $\pi\sigma^*$ states.¹⁶ If we use the S_z representation and symbolize the spin functions by Ω_m , we are interested in the emission from the states with $m = \pm 1$ since these are linear combinations of the $|x\rangle$ and $|y\rangle$ zero-field states. Because $R^1A_{2u}^0 = ^1A_{2u}^0$ and $R\Omega_m$

$= \omega^{-m}\Omega_m$, the emissive basis functions will be $|\Psi_{E_1^+}^0 \Omega_{-1}\rangle$ and $|\Psi_{E_1^-}^0 \Omega_{+1}\rangle$.

We can now write the transition moment matrix element for a transition of the $^3B_{1u}$ state to the ground state as

$$\langle \Psi(q; \rho, \varphi) \Omega_m \chi_{v,l} | e\hat{z} | ^1A_{1g}^0 \chi_{v',l'} \rangle. \quad (7)$$

Under the reasonable assumption that the spin-orbit coupling between the $^3E_{1u}$ and the $^1A_{2u}$ states is independent of ρ and φ , it follows by substitution of (6) into (7) and eliminating vanishing terms that the matrix element (7) is proportional to

$$\langle \lambda(\rho) ^1A_{2u}^0 e^{-im\varphi} \chi_{v,l} | e\hat{z} | ^1A_{1g}^0 \chi_{v',l'} \rangle. \quad (8)$$

In the pseudocylindrical approximation $\chi_{v,l}$ can be written as $\chi_{v,l} = R_{v,l|l'}(\rho) e^{il\varphi}$, and integration over φ then yields

$$\langle \lambda(\rho) ^1A_{2u}^0 R_{v,l|l'}(\rho) | e\hat{z} | ^1A_{1g}^0 R_{v',l'|l'}(\rho) \rangle \delta_{-m+l,l'} \quad (9)$$

$$\propto \langle R_{v,l|l'}(\rho) \lambda(\rho) R_{v',l'|l'}(\rho) \rangle \delta_{-m+l,l'}. \quad (10)$$

Because $m = \pm 1$, it follows that in the pseudocylindrical approximation ($l - l'$) is constrained to ± 1 . The significant aspect of the transition moment (10) is that the integrand, in addition to the Franck-Condon product $R_{v,l|l'}(\rho) R_{v',l'|l'}(\rho)$, contains an extra factor $\lambda(\rho)$.

In the calculation of Sec. III we did not work in the CBO approximation but obtained an electronic wave function for the lowest triplet state in which the $^3E_{1u}$ state is implicitly contained. To evaluate the matrix element (10) we would have to recover the coefficient $\lambda(\rho)$, i.e., the variation of the amount of mixing between the $^3B_{1u}$ and $^3E_{1u}$ states with ρ . Though a complete "unscrambling" is impossible, an approximate one can be achieved by considering the two main configurations in the wave functions of these states (see Fig. 1). The uncoupled wave functions are assumed to be properly described by

$$\begin{aligned} |B_{1u}\rangle^0 &= \frac{1}{\sqrt{2}} (|A\rangle + |Q\rangle), \\ |E_{1u}^a\rangle^0 &= \frac{1}{\sqrt{2}} (|A\rangle - |Q\rangle), \end{aligned} \quad (11)$$

in which $|E_{1u}^a\rangle$ is that component of E_{1u} which in the coupled case interacts with the B_{1u} state. Our calculations yield the wave function for the lowest triplet state in the form

$$|^3B_{1u}(\rho)\rangle = c_1(\rho)|A\rangle + c_2(\rho)|Q\rangle + \dots \quad (12)$$

Substitution of (11) into (12) and neglect of configurations other than $|A\rangle$ and $|Q\rangle$ then leads to

$$\begin{aligned} |^3B_{1u}(\rho)\rangle &= \mu(\rho) |^3B_{1u}\rangle^0 + \lambda(\rho) |^3E_{1u}^a\rangle^0, \\ \mu(\rho) &\equiv \frac{1}{\sqrt{2}} [c'_1(\rho) + c'_2(\rho)], \\ \lambda(\rho) &\equiv \frac{1}{\sqrt{2}} [c'_1(\rho) - c'_2(\rho)], \end{aligned} \quad (13)$$

in which c'_1 and c'_2 have been obtained as the normalized coefficients from c_1 and c_2 . The dependence of $\lambda(\rho)$ found in this way is depicted in Fig. 9. It is seen that $\lambda(\rho)$ varies very rapidly near $\rho = 0$ but becomes nearly constant for large values of ρ .

A calculation of the intensity ratios by means of (10)

FIG. 9. Variation with the $S_u(\rho, \varphi)$ symmetry coordinate of the contribution of the ${}^3E_{1u}$ state to the wave function of the ${}^3B_{1u}(\rho)$ state.

leads to the values given in the lower half of Table III. These values show that the inclusion of $\lambda(\rho)$ leads to an increase in the discrepancy between experiment and theory, though qualitatively the numbers are still in reasonable agreement.

C. Influence of a crystal field

After having considered the distortion in the ${}^3B_{1u}$ state of the free molecule, we will briefly turn to the experimental situation in which the benzene molecule is subjected to a crystal field. As we saw it is very likely that the energy differences in the trough of the free molecule are very small and the question remains to what extent the crystal field may "lock" the molecule in a specific form as has often been suggested. In order to obtain an idea of the order of magnitude of the energy differences the crystal field introduces into the potential-energy surface for the free molecule, we have performed a calculation for a C_6H_6 crystal.

In this calculation a lattice was built up according to the crystal structure given in Ref. 62 with one of the ground-state molecules replaced by a molecule with the geometry of an excited triplet-state molecule. The crystal-field energy then was calculated as the sum of the atom-atom interactions of this excited molecule with all ground-state molecules within a radius of 12 Å. The atom-atom potential between atoms n and m , separated by a distance r_{nm} , was represented by

$$V_{nm}(r_{nm}) = B_{nm}e^{(-C_{nm}r_{nm})} - A_{nm}r_{nm}^{-6}, \quad (14)$$

where the parameters A_{nm} , B_{nm} , and C_{nm} for C-C, C-H, and H-H interactions were given values according to Bonadeo and D'Alessio.⁶³ Any Coulomb interaction is neglected since in a crystal of the present type its contribution is an order of magnitude smaller than the sum of the other two terms.

The results of such a calculation for different conformations are given in Fig. 10. The energy differences in the trough introduced by the crystal field are of the order of 10 cm^{-1} and certainly much smaller than the energy of stabilization relative to the hexagonal conformation. Although the

FIG. 10. Crystal-field energy as a function of the distortion of the benzene molecule. The variations are given as contours; the numbers in the contours represent the energy in cm^{-1} . The zero of energy is defined as the crystal-field energy for a hexagonal molecule. The quinoidal conformations occur for $\varphi = 0, \pm 120^\circ$, the antiquinoidal ones for $\varphi = \pm 60^\circ, 180^\circ$.

values of the A, B, and C parameters used in Eq. (14) were those for the ground state, it is improbable that a calculation with parameter values adapted to the triplet state would change this conclusion significantly. Experimentally a splitting of the ($v = 1; l = \pm 1$) levels of 13 cm^{-1} is observed,¹¹ which supports the idea that the crystal-field energy differences are of a comparable order of magnitude.

As remarked in the Introduction, EPR experiments have shown that the "conformation" favored in a crystal field is not always the same but proves to be very host dependent.¹⁶⁻²¹ For some hosts one has previously concluded to a quinoidal conformation, for other hosts, on the contrary, to an antiquinoidal conformation. But, although the molecule in the ${}^3B_{1u}$ state is no longer stable in the D_{6h} conformation, the calculated vibrational wave function for the zero-point vibration shows that experimental quantities such as EPR parameters may not directly be related to a specific nuclear conformation. During the vibration the molecule makes large excursions over the complete energy surface and is not confined to the bottom of the trough. Hence a meaningful comparison of calculated quantities with experimental data should require an averaging over the vibrational wave function. While the free molecule looks hexagonal, the result of such an average in a solid will primarily depend on the crystal-field anisotropy and only to a lesser extent on small variations in energy of the bottom of the well which depend on ϕ with a periodicity of $2\pi/3$. The fact that one has to take an average over a wide range of geometries explains why the zero-field EPR parameter E —which reflects the nonhexagonality—has a much smaller value than has previously been calculated for fixed distorted geometries.^{4,36}

V. CONCLUDING REMARKS

The present calculations have shown that in a static picture the hexagonal conformation of benzene is not stable in the $^3B_{1u}$ state. The energy surface calculated for the S_8 distortion shows that it is surrounded by a wide, 800 cm^{-1} deep trough, and that the energy differences along the bottom of the trough, if existing at all, are very small. The calculation of the potential-energy surface of the $^1B_{1u}$ state reveals that this state should be subject to a similar distortion behavior, in accordance with Moffitt's original ideas^{1,2} about the distortion in the B_{1u} states.

A valid comparison with experimental results, however, can only be obtained in a dynamic picture. By solving the nuclear Schrödinger equation we have obtained various spectroscopic observables. The frequency of the ν_8 vibration in the $^3B_{1u}$ state is nicely recovered and shown to be primarily determined by the width and relative flatness of the bottom of the potential well. A calculation of relative intensities of vibronic bands qualitatively agrees with experimental results. The vibrational wave function of the zero-point vibration demonstrates that the molecule in this state is by no means confined to the trough but makes large excursions over the complete energy surface. The free molecule thus will appear hexagonal, but even a weak crystal field can explain the remarkable host-dependent effects observed in experiment. The crystal field will not, as previously thought, "lock" the molecule in a specific distorted conformation that is favored by intramolecular effects, but by favoring certain regions of conformational space over others it will lead to a slightly nonhexagonal behavior when the average over the zero-point motion is taken.

Now that the distortion of benzene in the B_{1u} states is understood, it is interesting to compare the influence of a crystal field with the influence of a substituent. For many substituted benzene molecules it has experimentally been determined that these are subject to a similar conformational instability in their lowest triplet state as benzene. Calculations on the lowest triplet state of p-xylene, in which the benzene nucleus is perturbed by two methyl substituents, have revealed that this molecule is distorted upon excitation into the lowest triplet state,⁶⁴ and that the influence of these substituents is even larger than previously expected.⁶⁴

Note added. After the submission of the present work a paper by Knowles *et al.* appeared⁶⁵ in which the virtues of the MRDCI method are confirmed by an extensive comparative analysis.

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