

The core-hole excitation spectrum of benzene: A symmetry-adapted CNDO/S equivalent-core study including "spin-symmetry breaking" configurations

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The core-hole excitation spectrum of benzene below 12.0 eV is calculated within a symmetry-adapted *first-order* configuration interaction approach based on the CNDO/S equivalent-core approximation. One-electron singlet excitation energies of the neutral molecule are shown to approximate the corresponding "singlet"-coupled doublet energies in the delocalized core-hole species. Intensities in accord with experiment are obtained within the sudden approximation by projecting the C_{2v} reduced-symmetry equivalent-core solutions out of the first-order delocalized description. The total core-hole excitation intensity below 12.0 eV is found to be largely attributable to three one-electron $\pi^* \leftarrow \pi$ excitations of singlet-coupled doublet character which are split into the observed number of features, with correspondingly observed strengths, by first-order configuration interaction with energetically degenerate excitations in the "triplet"-coupled doublet manifold—"spin-symmetry breaking configurations." The observed core-hole excitation satellite at 10.7 eV and the asymmetry on the high binding energy side of the well-resolved satellite at 8.3 eV are interpreted in terms of two excitations of ${}^1E_{2g}(\pi^* \leftarrow \pi)$ neutral molecule parentage. The assignment of these higher-energy features as ${}^1E_{2g}(\pi^* \leftarrow \pi)$ in origin provides further support for the numerous theoretical predictions and recent conclusions based on spectroscopic investigations for states of ${}^1E_{2g}$ symmetry at approximately 8.0 and 10.0 eV in neutral benzene.

I. INTRODUCTION

Recently Riga, Pireaux, and Verbist,¹ and Lunell and co-workers² reported the detailed XPS shake-up spectrum of benzene in the condensed and vapor phases, respectively. A comparison of the condensed and vapor phase spectra in Fig. 1 clearly demonstrates that the total number, relative intensities, and energies of the shake-up features in the 5–12 eV range are in excellent agreement; the satellites appearing at 5.9, 7.0, 8.3, and 10.7 eV, and labeled *II*, *III*, *IV*, and *V* respectively. Although the vapor phase spectrum of Lunell and co-workers² does not resolve feature *I*, the statistics indicated in their work does not exclude a weak emission at 4.2 eV comparable in intensity to that found by Riga *et al.*¹

Several studies have addressed the electronic character of the benzene shake-up spectrum below 12.0 eV. Riga and co-workers,¹ e.g., ventured an assignment on the basis of a direct correlation with optical excitation energies of neutral benzene. Satellites *II*–*V* were attributed to $\pi^* \leftarrow \pi$ valence orbital excitations of the core-hole species. The extremely weak, but nevertheless well resolved, feature at 4.2 eV in their condensed phase spectrum (satellite *I* in Fig. 1), however, was excluded from discussion. Lunell and co-workers² performed an equivalent-core calculation on benzene using a variant of the Pariser–Parr–Pople (PPP) π -electron technique including configuration interaction among one-electron excited states as a means of characterizing the four satellites *II*–*V*. Briefly, Lunell and co-workers² concluded from their computations, assuming a reduction in the symmetry of benzene from D_{6h} to C_{2v} , concomitant with creation of a $C(1s)$ core hole, that

the excitation energies and shake-up intensities obtained from the reduced symmetry solution characterized satellites *II*, *III*, and *IV*. Again, satellite *V* was tentatively identified as arising from a $\pi^* \leftarrow \pi$ excitation process. Ohta, Fujikawa, and Kuroda³ performed an equivalent-core computation on benzene using the all-valence-electron CNDO/2 formalism and obtained three dominant shake-up transitions based on the reduced C_{2v} symmetry solution. Ohta and co-workers³ noted that shake-up processes arising from $\sigma^* \leftarrow \sigma$ transitions did not significantly contribute to the benzene spectrum below 12.0 eV. Kosugi and Kuroda⁴ more recently applied the π -electron equivalent-core approximation to the shake-up spectrum of benzene using both the full (D_{6h}) delocalized approach and the reduced-symmetry (C_{2v}) localized solution with symmetry-adapted valence orbitals, and obtained three excitations with intensities $\geq 1.0\%$ which were correlated with processes *III*, *IV*, and *V*. Satellite *II* was tentatively identified as arising from processes involving coupling of the core hole to the triplet excitations of the neutral molecule ("spin-symmetry breaking" single excitations or "triplet"-coupled doublet transitions) which were not explicitly included in the computational scheme. Lunell and co-workers² as well as Ohta *et al.*³ similarly excluded such states from their studies.

All of the computational work on the core-hole excitation spectrum of benzene to date, therefore, have the following in common: (1) the total intensity below 12.0 eV is attributed to $\pi^* \leftarrow \pi$ excitation processes; (2) coupling of the core hole to the molecular triplet excitations was not formally considered; (3) satellite *I* was not identified as a distinct process; (4) satellite *V* was ex-

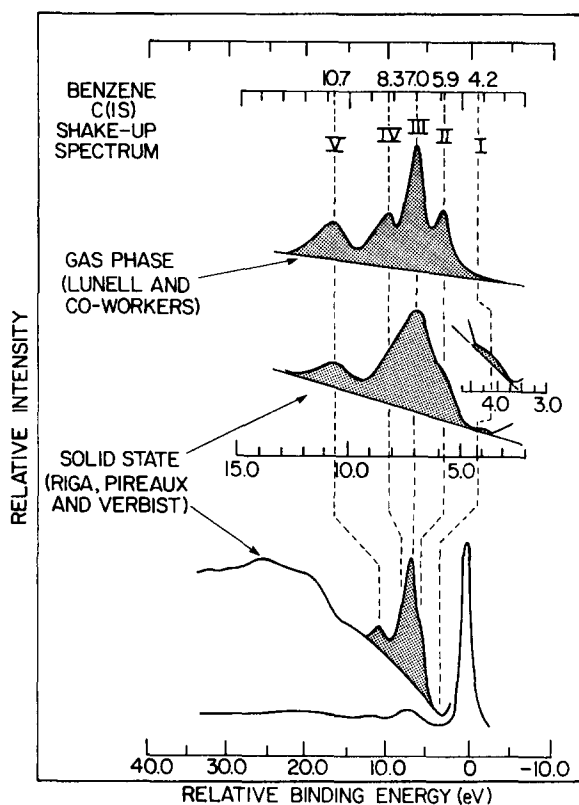


FIG. 1. A comparison of the condensed phase (Riga, Pireaux, and Verbist Ref. 1) and vapor phase (Lunell and co-workers Ref. 2) XPS satellite spectra of benzene for energies below 12.0 eV.

licitly rationalized as a $\pi^* \rightarrow \pi$ excitation; and (5) a maximum of three excitations of appropriate intensity (≥ 1.0 – $\sim 6.0\%$) appear below 12.0 eV.

The purpose of this work is to demonstrate within the framework of an all-valence-electron basis set that inclusion of both doublet state manifolds derived from coupling of the core-hole spin to valence-orbital excitations of singlet and triplet character (the singlet- and triplet-coupled doublet states, respectively) allows a consistent interpretation of the complete shake-up spectrum of benzene below 12.0 eV. In the following sections we present: (1) a short description of the computational method; (2) a comparison of the energetics of the excitation processes in the delocalized core-hole model and the neutral molecule; (3) a comparison of the localized equivalent-core computations with the delocalized description; and (4) estimates of the manifestations of configuration interaction between doublet states within a given manifold and between doublet states of singlet and triplet parentage. In the final section we present a summary of the conclusions which can be drawn from our work.

II. COMPUTATIONAL

The ground and excited states of the neutral and "ionized" molecules were obtained using the closed-shell all-valence-electron CNDO/S-CI program of Del Bene and Jaffé⁵ as developed by Ellis, Kuehnlenz, and Jaffé.⁶ The program was obtained from QCPE⁷ and used

without modification. Our application of this routine to benzene and related systems has been described previously.^{8,9}

The equivalent-core approximation^{10,11} permits a localized core hole to be simulated within a closed-shell framework by replacing the atom to be ionized (atomic number Z) by the atom following in the periodic table (atomic number $Z' = Z + 1$) and calculating the system as a closed-shell cation of charge $+1e$. Since valence-orbital excitations described by configuration interaction reflect potential changes in going from the $Z - (Z + 1)$ -system our results should "resemble" excitations in the actual final ionic system. Although other approximate MO schemes, assuming equivalent cores, have been used to address shake-up structure,¹² the CNDO/S-CI method appears particularly successful in this regard for systems containing first-row atoms.^{13,14} The problems arising from the fact that excitations relative to the closed-shell ($Z + 1$)-systems remain classified according to singlet and triplet parentage and, consequently, do not directly correspond to the doublet states of interest will be addressed in the following sections.

Excited states were generated from the CNDO/S ground state occupied and virtual orbitals through a configuration interaction procedure among the sixty lowest one-electron excitations. Nishimoto-Mataga integrals¹⁵ were selected to approximate the two-center electron-electron interaction terms.

III. RESULTS AND DISCUSSION

A. Localized versus delocalized description of the $C(1s)$ core-hole

As noted by Snyder¹⁶ and later demonstrated by Bagus and co-workers¹⁷ a core hole created within a homonuclear diatomic molecule, e.g., can be considered localized on a single center rather than delocalized over the whole molecule. In terms of molecular symmetry Bagus *et al.*¹⁷ calculated a single-determinant solution to the localized problem by recognizing the restrictions imposed on the Hartree-Fock solution by the full molecular symmetry. This does not imply, however, that the ionization process itself reduces the full molecular symmetry relative to the neutral system; providing, of course, that the nuclei remain fixed (Born-Oppenheimer approximation). Once the localized solution is found the symmetry-adapted solution is degenerate according to the number of symmetry equivalent atoms.^{4,17(b),18} Thus, it is always possible to form linear combinations which then transform within the full symmetry of the molecule. If we exclude vibrational coupling or Jahn-Teller distortions, which can reduce the symmetry,¹⁹ it is therefore reasonable to classify the ion-states within the point group of the neutral molecule.

Applying such arguments to the core-ionization of benzene yields six degenerate $C(1s)$ hole states which must be linearly combined to yield six symmetry-adapted solutions transforming as a_{1g} , e_{1u} , e_{2g} , and b_{1u} , Fig. 2. The splitting between these states is probably of the order of ≤ 0.1 eV^{17(b),20} which is presently beyond experi-

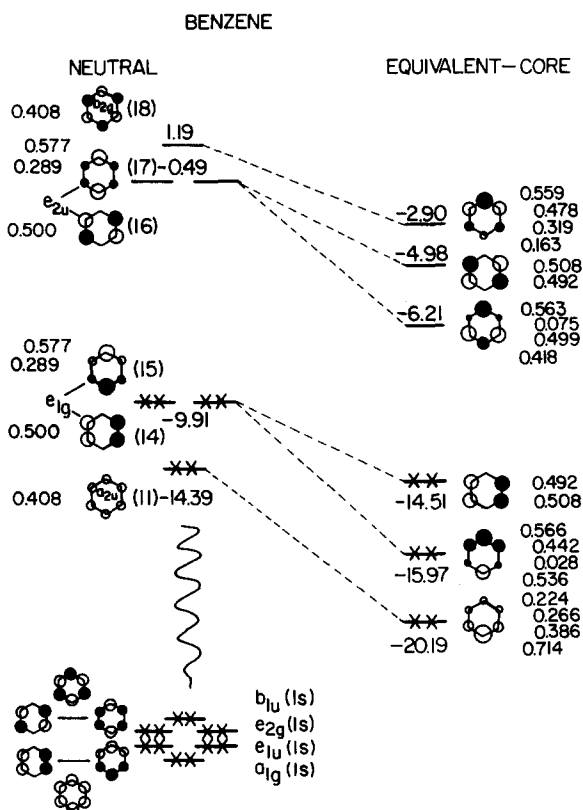


FIG. 2. A schematic representation of the neutral benzene orbitals of interest (D_{6h} symmetry) as viewed from above the molecular plane together with a representation of the response of the π orbitals to a localized core hole (C_{2v} symmetry) as approximated by the equivalent-core method. Atomic orbital coefficients are also given where the shaded or open orbital lobes denote the relative signs.

mental resolution. Symmetry-adapting the valence orbitals of benzene obtained from a localized solution (an equivalent-core computation, e.g.) to the D_{6h} point group of the initial system of course regenerates orbitals paralleling those of the neutral molecule.

To emphasize the complexities contained in the fully delocalized problem it is advantageous to examine the delocalized solutions in terms of symmetry selection rules for shake-up excitation. Transitions are allowed in the monopole approximation,^{21,22}

$$I\alpha \langle {}^2\Psi_F^{N-1} | a_h | {}^1\Psi_0^N \rangle|^2, \quad (1)$$

only if the symmetries of the initial and final states are equal. In Eq. (1) ${}^2\Psi_F^{N-1}$ is the final configuration interaction state of the ion, ${}^1\Psi_0^N$ is the ground state of the neutral molecule calculated at a similar level of accuracy, and a_h is the annihilation operator creating the core hole in orbital ϕ_h while leaving all other levels in ${}^1\Psi_0^N$ unchanged. Allowing for first-order configuration interaction among the various frozen-orbital configurations, which for one-electron valence excitation gives, e.g.,

$${}^2\psi_{ij}^{1,3}(k) = \sum^{i,j'} C_{ij'}^2 \Phi_{ij'}^{1,3}(k), \quad (2)$$

where ${}^2\Phi_{ij'}^{1,3}(k)$ and ${}^2\Phi_{ij'}^{3,3}(k)$ arise from the two different ways of coupling the spin of the valence electrons to that

of the core hole,^{23,24} the final ionic state can be written in terms of contributions from various core-hole, singly excited, doubly excited, etc. configurations obtained by *second-order* configuration interaction subject to appropriate symmetry constraints,

$$\begin{aligned} {}^2\Psi_F^{N-1}(D_{6h}) = & a_0^2 \psi_0(k) + \sum^{i,j'} b_{ij'}^1 {}^2\psi_{ij'}^1(k) \\ & + \sum^{i,j'} b_{ij'}^3 {}^2\psi_{ij'}^3(k) + \sum^{i,j'} b_{ij'}^{i,j'} {}^2\psi_{ij'}^{i,j'}(k) \\ & + \sum^{i,j',k,k'} b_{ij'k'}^{kk'} {}^2\psi_{ij'k'}^{kk'}(k) + \dots \end{aligned} \quad (3)$$

In terms of the D_{6h} multiplication table²⁵ one can in principle generate at least the 120 excited states noted in Table I *within each spin manifold* from coupling singly excited valence excitations derived from the π -orbital framework and the highest-lying occupied and lowest-lying virtual σ orbitals [the $e_{2g}(\sigma)$ and $b_{1u}(\sigma^*)$ levels, respectively] to the six approximately degenerate delocalized core holes. One finds from Table I that only one-electron promotions yielding a direct product containing E_{2g} are formally allowed. In the present context the allowed E_{2g} configuration is defined as an orbital symmetry-breaking configuration, ${}^{18}(a)$, ${}^{18}(e)$, ${}^{18}(f)$ i. e., one which is forbidden in the neutral species, but allowed in the ion by coupling to a core hole of appropriate symmetry. In terms of one-electron excitations E_{2g} transition symmetry can only be achieved through π -orbital excitation from the $a_{2u}(\pi)$, or to the $b_{2g}(\pi^*)$ orbital, Fig. 2. These excitations appear in the neutral molecule computation at energies several eV above the most intense experimental shake-up positions.⁸ We therefore arrive at the conclusion of Kosugi and Kuroda⁴ that the benzene shake-up intensity is negligible to *first-order* in the delocalized description.

Three additional coupling or excitation mechanisms can be constructed which confer "allowedness" to monopole transitions formally forbidden to first order. First, the E_{2g} core-hole excitation created, for example, by coupling the one-electron E_{1u} valence excitation with the b_{1u} core hole can interact by configuration interaction with the formally allowed E_{2g} one-electron process. The second and third mechanisms occur by including higher-order orbital symmetry-breaking configurations; i. e., doubly excited core-hole states.^{18(a)}, ${}^{18}(e)$, ${}^{18}(f)$ For example, ${}^2\psi_{ij'k'}^{kk'}(k)$ constructed by a concomitant one-electron $e_{2u}(\pi^*) \rightarrow e_{1g}(\pi)$ valence transition and a one-electron $e_{1u}(k) \rightarrow e_{2g}(k')$ core-hole excitation yields 21 additional states, 11 of which are formally monopole allowed. Furthermore, due to the approximate energetic degeneracy between the core holes these excitations will, within the same approximation, be energetically degenerate with the one-electron valence-orbital transitions! In addition, the wave function $\psi_{ij'k'}^{i,j'}(N)$ generated by a double $e_{2u}(\pi^*) \rightarrow e_{1g}(\pi)$ excitation yields $3A_{1g} + 3A_{2g} + 5E_{2g}$ configurations, each of which can couple to the $a_{1g} + b_{1g} + e_{2g} + e_{1u}$ core holes to give ${}^2\psi_{ij'k'}^{i,j'}(k)$, an addition of 64 configurations, 28 of which are allowed in the monopole approximation. The energies of doubly excited valence transitions, however, are expected to be significantly greater than those of the corresponding

TABLE I. The states generated by coupling the one-electron valence excitations generated between the $a_{2u}(\pi)$, $e_{2g}(\pi)$, $e_{1g}(\pi)$, $e_{2u}(\pi^*)$, $b_{2g}(\pi^*)$, and $b_{1u}(\sigma^*)$ orbitals to the six symmetry-adapted core holes shown in Fig. 2. The orbital transition character is indicated along with the calculated energy (eV) of the corresponding singlet configuration interaction excitation in the neutral molecule.

$(\phi_i) \rightarrow (\phi_{j'})$	$(\Gamma_i \otimes \Gamma_{j'})$	$\otimes \Gamma_k =$	Γ_F	${}^1\tilde{E}_{ij'}(N)$
(14, 15) \rightarrow (16, 17) (12, 13) \rightarrow (19)	E_{1u} (6.79) (11.29)	$\otimes \begin{Bmatrix} b_{1u} \\ e_{2g} \\ e_{1u} \\ a_{1g} \end{Bmatrix}$	$= \begin{Bmatrix} E_{2g} \\ B_{1u} + B_{2u} + E_{1u} \\ A_{1g} + A_{2g} + E_{2g} \\ E_{1u} \end{Bmatrix}$	(5.88, 6.51) (11.19)
(14, 15) \rightarrow (19) (12, 13) \rightarrow (16, 17)	E_{2u} (7.62) (6.68)	$\otimes \begin{Bmatrix} b_{1u} \\ e_{2g} \\ e_{1u} \\ a_{1g} \end{Bmatrix}$	$= \begin{Bmatrix} E_{2u} \\ B_{1g} + B_{2g} + E_{1g} \\ B_{1u} + B_{2u} + E_{2u} \\ E_{1g} \end{Bmatrix}$	(8.03) (6.89) ^a
(12, 13) \rightarrow (18)	E_{1g} (8.04) ^b	$\otimes \begin{Bmatrix} b_{1u} \\ e_{2g} \\ e_{1u} \\ a_{1g} \end{Bmatrix}$	$= \begin{Bmatrix} E_{2u} \\ B_{1g} + B_{2g} + E_{1g} \\ A_{1u} + A_{2u} + E_{2u} \\ E_{1g} \end{Bmatrix}$	(9.26)
(14, 15) \rightarrow (18) (11) \rightarrow (16, 17)	E_{2g} (7.99) (10.01)	$\otimes \begin{Bmatrix} b_{1u} \\ e_{2g} \\ e_{1u} \\ a_{1g} \end{Bmatrix}$	$= \begin{Bmatrix} E_{1u} \\ A_{1g} + A_{2g} + E_{2g} \\ B_{1u} + B_{2u} + E_{1u} \\ E_{2g} \end{Bmatrix}$	(8.09) (10.20)
(14, 15) \rightarrow (16, 17) (11) \rightarrow (18)	B_{1u} (6.10) (12.32)	$\otimes \begin{Bmatrix} b_{1u} \\ e_{2g} \\ e_{1u} \\ a_{1g} \end{Bmatrix}$	$= \begin{Bmatrix} A_{1g} \\ E_{1u} \\ E_{2g} \\ B_{1u} \end{Bmatrix}$	(5.88, 6.51) (12.32)
(14, 15) \rightarrow (16, 17)	B_{2u} (4.84)	$\otimes \begin{Bmatrix} b_{1u} \\ e_{2g} \\ e_{1u} \\ a_{1g} \end{Bmatrix}$	$= \begin{Bmatrix} A_{1g} \\ E_{1u} \\ E_{2g} \\ B_{2u} \end{Bmatrix}$	(5.88, 6.51)
(11) \rightarrow (19)	B_{2g} (13.11)	$\otimes \begin{Bmatrix} b_{1u} \\ e_{2g} \\ e_{1u} \\ a_{1g} \end{Bmatrix}$	$= \begin{Bmatrix} A_{2u} \\ E_{1g} \\ E_{2u} \\ B_{2g} \end{Bmatrix}$	(12.51)
(12, 13) \rightarrow (16, 17)	A_{1u} (6.61)	$\otimes \begin{Bmatrix} b_{1u} \\ e_{2g} \\ e_{1u} \\ a_{1g} \end{Bmatrix}$	$= \begin{Bmatrix} B_{1g} \\ E_{2u} \\ E_{1g} \\ A_{1u} \end{Bmatrix}$	(6.89) ^a
(12, 13) \rightarrow (16, 17)	A_{2u} (6.90)	$\otimes \begin{Bmatrix} b_{1u} \\ e_{2g} \\ e_{1u} \\ a_{1g} \end{Bmatrix}$	$= \begin{Bmatrix} B_{2g} \\ E_{2u} \\ E_{1g} \\ A_{2u} \end{Bmatrix}$	(6.89) ^a

^a $K_{\sigma\sigma^*}$ is identically zero in ZDO approximations.

^bSignificant configuration interaction with higher-lying excitations.

one-electron excitations²⁶ and, consequently, should contribute less strongly to ${}^2V_F^{N-1}$.²⁷

The near degeneracy of ${}^2\Phi_{ij'}^1(k)$ and ${}^2\Phi_{ij'}^3(k)$ particular to benzene, as discussed below, further compounds the configuration interaction problem. We conclude that due to the density of symmetry-allowed excitations in the delocalized solution the concept of a strict set of symmetry selection rules is meaningless or ill-defined at best.

B. Valence-orbital excitations in the neutral and ionized species

In light of the above arguments we seek suitable approximations which render the benzene problem tractable, but which retain sufficient detail to elucidate the

primary interactions and coupling mechanisms. Within this context it is first useful to compare excitations in the ion with those in the neutral molecule more closely. In terms of the beginning N electron closed-shell molecule an electronic excitation from orbital ϕ_i to orbital $\phi_{j'}$ leads to one-electron singlet and triplet configurations with energies,²⁸

$${}^1\tilde{E}_{ij'}(N) = \epsilon_{j'} - \epsilon_i - J_{ij'} + 2K_{ij'} \quad (4)$$

and

$${}^3\tilde{E}_{ij'}(N) = \epsilon_{j'} - \epsilon_i - J_{ij'} \quad (5)$$

where ϵ_i and $\epsilon_{j'}$ are the occupied and virtual Hartree-Fock orbital energies, and $J_{ij'}$ and $K_{ij'}$ are the Coulomb and exchange integrals, respectively. Within the basis set of the neutral molecule the energies of the "singlet"-

TABLE II. π -orbital overlap matrix between the indicated levels of the neutral and the symmetry-reduced (C_{2v}) equivalent-core species of benzene.

		Equivalent-core ($Z+1$)							
		$\phi_{18}^L (4b_1)$	$\phi_{17}^L (3b_1)$	$\phi_{16}^L (2a_2)$	$\phi_{15}^L (2b_1)$	$\phi_{14}^L (1a_2)$	$\phi_{11}^L (1b_1)$	$\sum C^L ^2$	
Neutral molecule	$b_{2g} (\pi^*) - \phi_{18}^S (b_1)$	-0.945	0.287	0.000	-0.112	0.000	-0.102	0.998	
	$e_{2u} (\pi^*)$	$\phi_{17}^S (b_1)$	-0.321	-0.897	0.000	0.253	0.000	0.164	0.999
		$\phi_{16}^S (a_2)$	0.000	0.000	1.000	0.000	0.000	0.000	1.000
	$e_{1g} (\pi)$	$\phi_{15}^S (b_1)$	0.043	-0.329	0.000	-0.875	0.000	-0.352	1.000
		$\phi_{14}^S (a_2)$	0.000	0.000	0.000	0.000	1.000	0.000	1.000
	$a_{2u} (\pi) - \phi_{11}^S (b_1)$	-0.031	0.067	0.000	-0.396	0.000	0.914	0.998	

coupled doublet ${}^2\Phi_{ij}^1(k)$, and the "triplet"-coupled doublet ${}^2\Phi_{ij}^3(k)$, formed by coupling the valence electron spins to the core hole²⁹ are given by ($\epsilon_k = 0$),^{23,30}

$${}^2\bar{E}_{ij}^1(k) = [(\epsilon_j - J_{j,k}) - (\epsilon_i - J_{i,k}) - J_{ij}] + 2K_{ij} - 1/2K_{ik} + 1/2K_{j,k} \quad (6)$$

and

$${}^2\bar{E}_{ij}^3(k) = [(\epsilon_j - J_{j,k}) - (\epsilon_i - J_{i,k}) - J_{ij}] + 1/2K_{ik} + 3/2K_{j,k}, \quad (7)$$

where the terms have been arranged to provide maximum coincidence with corresponding elements of the closed-shell system. J_{ik} , $J_{j,k}$, K_{ik} , and $K_{j,k}$ are the indicated core-valence interaction integrals, and $\epsilon_j - J_{j,k}$ and $\epsilon_i - J_{i,k}$ are approximations to the respective eigenvalues of the ionic system. Due to spin-selection rules the quartet state is not populated.

The delocalized core-hole structure of Fig. 2 has the clear advantage that when the potential changes in going from the neutral to the *symmetry-adapted* ionic species are averaged over the six nearly equivalent core-hole configurations $J_{ik} \approx J_{j,k}$ and $K_{ik} \approx K_{j,k} = K_k^{avg}$. Perturbation to the orbitals of interest due to the average core-hole configuration can be considered as an addition of $1/6\epsilon$ to the diagonal carbon terms in the Hartree-Fock matrix resulting in a nearly *uniform* displacement of the benzene valence levels to higher binding energy.³¹ We therefore consider the valence orbitals and eigenvalue *differences* of the ionized species to be equivalent to those of the neutral molecule. Substituting the above average values for J_{ik} , $J_{j,k}$, K_{ik} , and $K_{j,k}$ into Eqs. (6) and (7) yields,

$${}^2\bar{E}_{ij}^1(k) = \epsilon_j - \epsilon_i - J_{ij} + 2K_{ij}, \quad (8)$$

and

$${}^2\bar{E}_{ij}^3(k) = \epsilon_j - \epsilon_i - J_{ij} + 2K_k^{avg}, \quad (9)$$

or

$${}^2\bar{E}_{ij}^3(k) = {}^2\bar{E}_{ij}^1(k) + 2(K_k^{avg} - K_{ij}). \quad (10)$$

The splitting between ${}^2\Phi_{ij}^1(k)$ and ${}^2\Phi_{ij}^3(k)$, therefore, does not necessarily parallel the singlet-triplet splitting of the neutral molecule as is often assumed. In fact, in the present case ${}^2\bar{E}_{ij}^3(k) > {}^2\bar{E}_{ij}^1(k)$ for $K_{ik}(K_{j,k}) > K_{ij}$. K_{ik} and $K_{j,k}$ will in general differ from K_{ij} ,

due to the difference in basis functions. The splitting of the $N(1s)$ ionization in the free NO molecule was shown to arise from a one-center core-valence exchange interaction determined experimentally to be ~ 1.2 eV.³² This compares favorably to the *average* value of K_{ij} (K_{ij}^{avg}) calculated from the four neutral benzene one-electron excitations of $e_{2u}(\pi^*) - e_{1g}(\pi)$ parentage using the CNDO/S parametrization ($K_{ij}^{avg} = 1.12$ eV using Nishimoto-Mataga integrals; $K_{ij}^{avg} = 0.85$ eV for Pariser-Parr integrals³³). Thus to first order in the frozen-orbital approximation we assume for an "averaged" configuration that,

$$\left. \begin{array}{l} {}^2\bar{E}_{ij}^1(k) \\ {}^2\bar{E}_{ij}^3(k) \\ {}^1\bar{E}_{ij}(N) \end{array} \right\} \approx \epsilon_j - \epsilon_i - J_{ij} + 2K_{ij}. \quad (11)$$

In the absence of configuration interaction we must contend with a dual manifold of doublet excitations approximately degenerate in energy to that of the corresponding singlet states of the neutral system.^{34,35}

The problem can now be reduced to one involving only several one-electron excitations by projecting the localized equivalent-core contributions out of the first-order delocalized solution. Figure 2 gives the results of the localized ($Z+1$) calculation, showing only the perturbations to the π -orbital manifold, from which the symmetry-adapted orbitals are obtained according to,²⁵

$$\phi^S(\Gamma_{D_{6h}}) = \sum_I C_I^L \phi^L(\Gamma_{C_{2v}}), \quad (12)$$

where $C_I^L = \langle \phi^S(\Gamma_{D_{6h}}) | \phi_I^L(\Gamma_{C_{2v}}) \rangle$. The expansion coefficients (C_I^L) are tabulated for π orbitals in Table II and for selected σ orbitals in Table III. Intensities are assigned in the *delocalized* description based on Eq. (1). Appropriate wave function expansion and integration over spin orbitals give,

$${}^2I_{ij}^1, \alpha | 2^{1/2} C_I^L \langle D_i^N | D_j^{Z+1} \rangle |^2, \quad (13)$$

where $\langle D_i^N | D_j^{Z+1} \rangle$ is the overlap of the determinants formed when D_i^N spans all occupied orbitals and D_j^{Z+1} is constructed by replacing ϕ_i by ϕ_j .^{17(b),36} Within our approximation ${}^2I_{ij}^3$ is identically zero.^{14(b),37} In the present case D_i^N and D_j^{Z+1} were limited to π_{11} , σ_{12} , σ_{13} ,

TABLE III. σ -orbital overlap matrix (including hydrogen atom coefficients) between the indicated levels of the neutral and the symmetry-reduced (C_{2v}) equivalent-core species of benzene.

		Equivalent-core ($Z+1$)									
		ϕ_{24}^L ($7b_2$)	ϕ_{23}^L ($11a_1$)	ϕ_{22}^L ($10a_1$)	ϕ_{21}^L ($6b_2$)	ϕ_{20}^L ($9a_1$)	ϕ_{19}^L ($8a_1$)	ϕ_{13}^L ($5b_2$)	ϕ_{12}^L ($7a_1$)	$\sum C^L ^2$	
Neutral molecule	e_{1u} (σ^*)	ϕ_{24}^S (b_2)	0.977	0.000	0.000	0.174	0.000	0.000	0.014	0.000	0.985
		ϕ_{23}^S (a_1)	0.000	0.831	0.533	0.000	-0.019	-0.008	0.000	-0.009	0.975
	a_{1g} (σ^*)	ϕ_{22}^S (a_1)	0.000	-0.537	0.835	0.000	-0.077	0.062	0.000	0.008	0.995
		ϕ_{21}^S (b_2)	0.173	0.000	0.000	0.983	0.000	0.000	0.032	0.000	0.997
	e_{2g} (σ^*)	ϕ_{20}^S (a_1)	0.000	-0.019	0.066	0.000	0.965	0.227	0.000	0.013	0.988
		ϕ_{19}^S (a_1)	0.000	0.090	-0.061	0.000	-0.229	0.965	0.000	-0.021	0.944
	b_{1u} (σ^*)	ϕ_{13}^S (b_2)	0.015	0.000	0.000	0.058	0.000	0.000	-0.957	0.000	0.919
		ϕ_{12}^S (a_1)	0.000	-0.016	-0.022	0.000	0.020	0.059	0.000	0.972	0.949

π_{14} , and π_{15} (Tables II and III). Off-diagonal elements of all underlying terms were assumed negligible. The projected intensities for the excitations of interest are given in Table IV. We obtain *three* one-electron $\pi^* \rightarrow \pi$ excitations in the delocalized description with $I_{ij} > 1.5\%$, whereas $\sigma^* \rightarrow \sigma$ excitation is computed to have negligible intensity below 14.0 eV. Intensities obtained by assuming $C_1^L = 1.0$ for the largest contributors and zero otherwise are given in parenthesis. Without wave function projection our one-electron relative intensities are essentially identical to those of Lunell and co-workers.² The redistribution of π -electron intensity obtained by the projection technique occurs since excitation ${}^2\phi_{15,17}(k)$, contracted here to (15, 17), in the localized description, e.g., contributes to (15, 17) and (15, 18) in the delocalized basis set. It should be emphasized that much of the substantial intensity attributed to (11, 17) in Table IV arises from "secondary" coupling terms in the determinantal overlap, "ground state correlation" contributions in the nomenclature of Martin and Shirley,³⁶ rather than from the single $\langle \pi_{11}^N | \pi_{17}^{Z+1} \rangle$ projection which establishes the parentage. $\langle D_i^N | D_{17}^{Z+1} \rangle$ reduces to

$$\langle D_i^N | D_{17}^{Z+1} \rangle = \langle \pi_{11}^N | \pi_{15}^{Z+1} \rangle \langle \pi_{15}^N | \pi_{17}^{Z+1} \rangle - \langle \pi_{11}^N | \pi_{17}^{Z+1} \rangle \langle \pi_{15}^N | \pi_{15}^{Z+1} \rangle.$$

The first product gives 0.189, whereas the second term containing $\langle \pi_{11}^N | \pi_{17}^{Z+1} \rangle$ yields only 0.059. Assuming simple overlaps between π_i^N and π_j^{Z+1} yields ${}^2I_{(15,17)}^1 = 21.50\%$ and ${}^2I_{(11,17)}^1 = 0.89\%$. Ground-state correlation, therefore, not only enhances ${}^2I_{(11,17)}^1$ by an order of magnitude, but decreases ${}^2I_{(15,17)}^1$ by a factor of 2. Similar effects were apparently calculated by Ohta *et al.*,³ and Lunell and co-workers,² the latter of which also obtained $I_{(11,17)} = 7.0\%$ from determinantal projection of the reduced symmetry species. Evaluation of ${}^2I_{(11,17)}^1$ using the molecular orbital coefficients of Lunell *et al.*² and assuming simple orbital overlap yields ${}^2I_{(11,17)}^1 \sim 0.4\%$.

C. Manifestations of configuration interaction between doublet manifolds

The final-state configuration interaction problem by which the intensities are further redistributed can be

considerably reduced by examining the interaction matrix elements between various one-electron excitations. Those of interest are given in Table V. Pertinent to the present problem is: (1) the interaction energy between singlet-coupled doublets is identical to that between corresponding singlet excitations in the neutral molecule, full symmetry restrictions remain imposed since the matrix element for interaction does not include core-valence terms; (2) interaction between doublet manifolds is identically zero when both occupied and virtual orbital indices differ; (3) interaction between doublet manifolds is negligible when both indices are

TABLE IV. The calculated one-electron singlet excitation energies of neutral benzene and the shake-up intensities obtained by symmetry-adapting the C_{2v} equivalent-core results to the D_{6h} point group. $\langle D_i^N | D_{j'}^{Z+1} \rangle$ was constructed from appropriate elements of the π and σ overlap matrices given in Tables II and III.

Transition (i, j')	Energy (eV)	Intensity (%)
$\pi^* \rightarrow \pi$		
(14, 17)	5.88	
(15, 16)	5.88	
(14, 16)	6.51	
(15, 17)	6.51	12.27 (15.25)
(14, 18)	8.09	
(15, 18)	8.09	1.99 (0.14)
(11, 16)	10.20	
(11, 17)	10.20	5.73 (7.12)
(11, 18)	12.32	0.30 (0.34)
$\sigma^* \rightarrow \sigma$		
(12, 19)	11.19	(0.55)
(13, 19)	11.19	
(12, 21)	11.92	
(13, 20)	11.92	
(12, 20)	12.15	(0.06)
(13, 21)	12.15	(0.55)
(12, 22)	13.37	(0.08)
(13, 22)	13.37	
(12, 23)	13.63	(0.04)
(13, 23)	13.63	
(12, 24)	> 14.00	
(13, 24)	> 14.00	(0.04)

TABLE V. The matrix elements for interaction between the indicated one-electron excitations where $(l j' \| m' i)$, $(l j' \| i m')$, etc., are the exchange ($K_{l j' m' i}$) and Coulomb ($J_{l j' i m'}$) integrals, respectively. The neutral molecule matrix elements are those of Pople,^a and Lowitz,^b whereas the matrix elements between doublets are those of Guest and co-workers (Ref. 29). The matrix elements for doublet interaction were derived from a basis function expansion in terms of the neutral molecule, and consequently, differ slightly from those obtained relative to an explicit open-shell hole-state calculation, Zahradnik and Carsky^c.

$$\begin{aligned} \langle {}^1\Phi_{ij'}(N) | H | {}^1\Phi_{im'}(N) \rangle &= 2(l j' \| m' i) - (l j' \| i m') \\ \langle {}^3\Phi_{ij'}(N) | H | {}^3\Phi_{im'}(N) \rangle &= -(l j' \| i m') \\ \langle {}^2\Phi_{ij'}^1(k) | H | {}^2\Phi_{im'}^1(k) \rangle &= 2(l j' \| m' i) - (l j' \| i m') \\ \langle {}^2\Phi_{ij'}^3(k) | H | {}^2\Phi_{im'}^3(k) \rangle &= -(l j' \| i m') + (k j' \| m' k) \delta_{ii} + (k l \| i k) \delta_{j'm'} \\ \langle {}^2\Phi_{ij'}^1(k) | H | {}^2\Phi_{im'}^3(k) \rangle &= 3/\sqrt{12} \{ (k l \| i k) \delta_{j'm'} - (k j' \| m' k) \delta_{ii} \} \end{aligned}$$

^aJ. A. Pople, Proc. Phys. Soc. (London) 68A, 81 (1955).

^bD. A. Lowitz, J. Chem. Phys. 46, 4698 (1967).

^cR. Zahradnik and P. Carsky, Proc. Phys. Org. Chem. 10, 327 (1973).

identical ($K_{ik} \approx K_{j'n}$), and (4) interaction between doublet manifolds is significant in benzene (delocalized structure) when either the initial or final orbital indices of the interacting states coincide. It should be emphasized that symmetry restrictions in the valence manifold are relaxed for interaction between singlet- and triplet-coupled doublets since the interaction term does not contain elements with mixed occupied and virtual orbital indices.

Also, the one-electron singlet-coupled doublet excitations of $e_{2u}(\pi^*) - e_{1g}(\pi)$ parentage occur in degenerate pairs with ${}^2\bar{E}_{14,17}^1(k) = {}^2\bar{E}_{15,16}^1(k) = 5.88$ eV with $K_{ij'}$ = 0.72 eV, and ${}^2\bar{E}_{14,16}^3(k) = {}^2\bar{E}_{15,17}^3(k) = 6.51$ eV with $K_{ij'}$ = 1.50 eV. Assuming, in line with the above arguments, that $K_k^{avg} \approx K_{ij'}^{avg}$ we obtain from Eq. (10),

$$\left. \begin{aligned} {}^2\bar{E}_{14,17}^1(k) \\ {}^2\bar{E}_{15,16}^1(k) \\ {}^2\bar{E}_{14,16}^3(k) \\ {}^2\bar{E}_{15,17}^3(k) \end{aligned} \right\} \approx 5.88 \text{ eV}; \quad \left. \begin{aligned} {}^2\bar{E}_{14,16}^1(k) \\ {}^2\bar{E}_{15,17}^1(k) \\ {}^2\bar{E}_{14,17}^3(k) \\ {}^2\bar{E}_{15,16}^3(k) \end{aligned} \right\} \approx 6.51 \text{ eV}.$$

The "spin-symmetry breaking" configurations become approximately degenerate with the singlet-coupled doublets with which they are permitted to interact further enhancing the effective coupling (splitting). All interaction matrix elements not directly involving summations over ϕ_k are extracted from the neutral molecule singlet- and triplet-manifold excitation energies (magnitudes) and wave functions (signs) given in Tables IV and VI and Ref. 8. The magnitude of coupling between manifolds requires evaluation of exchange terms involving summation over three indices. In accord with the above arguments for the $e_{2u}(\pi^*) - e_{1g}(\pi)$ excitations a typical element is

$$\begin{aligned} K_{1j'j'i} &= 3/\sqrt{12} (kl \| ik) \\ &= 0.866 \langle \phi_{1s}(1) \phi_i(2) | r_{12}^{-1} | \phi_i(1) \phi_{1s}(2) \rangle. \end{aligned}$$

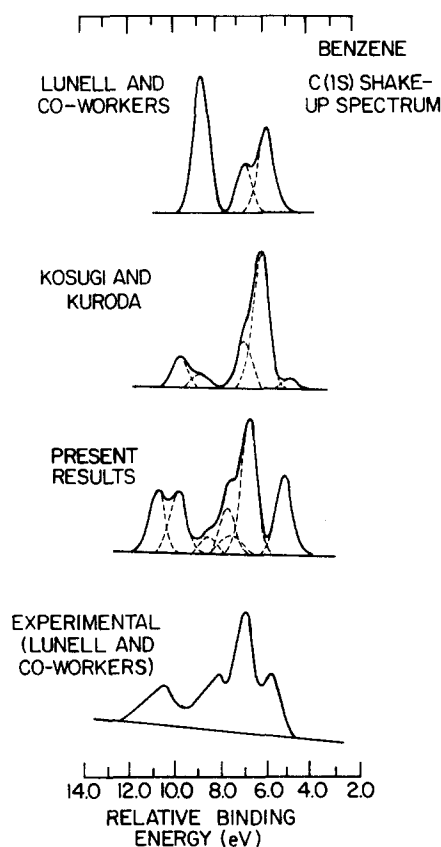


FIG. 3. Comparisons of the calculated benzene shake-up structure of Lunell and co-workers, (Ref. 2) Kosugi and Kuroda (Ref. 4) and the present results with the experimental spectrum. Each indicated transition is represented by a Gaussian distribution of full-width at half-maximum (FWHM) of 0.8 eV and normalized in accord with the calculated relative intensities.

Expansion in terms of LCAO coefficients yields,

$$K_{1j'j'i} = 0.866 \sum_{\mu}^A \sum_{\nu}^B C_{\mu\nu} C_{i\nu} C_{i\mu} C_{\mu\nu} \langle \chi_{1s}(1) \chi_{2p}(2) | r_{12}^{-1} | \chi_{2p}(1) \chi_{1s}(2) \rangle,$$

where μ and ν are atomic orbital indices on atoms A

TABLE VI. The calculated singlet configuration interaction energies and wave functions of interest for neutral benzene. Corresponding properties of the triplet manifold have been previously tabulated in Ref. 8 where the computations are also compared with experiment.

	Symmetry	Energy (eV)	Wave function
1	${}^1B_{2u}$	4.84	0.707 (15, 16) + 0.707 (14, 17)
2	${}^1B_{1u}$	6.10	0.707 (15, 17) - 0.707 (14, 16)
3	${}^1E_{1u}$	6.79	{ 0.689 (15, 17) + 0.698 (14, 15) 0.696 (15, 16) - 0.697 (14, 17)
4	${}^1E_{2g}$	7.98	{ -0.987 (15, 18) 0.987 (14, 18)
5	${}^1E_{2g}$	10.01	{ 0.954 (11, 17) 0.954 (11, 16)
6	${}^1B_{1u}$	12.32	1.000 (11, 18)

TABLE VII. The benzene π -electron configuration interaction matrix to be diagonalized to generate the final-state shake-up energies and intensity distribution. Off-diagonal elements along the diagonal blocks were extracted from the neutral molecule results, whereas $(k'l||ik)$ and $(kj'l||m'k)$ were estimated from the apparent experimental splittings given in Fig. 1.

		"SCD"							"TCD"										
		(14,17)	(15,16)	(14,16)	(15,17)	(15,18)	(14,18)	(11,16)	(11,17)	(11,18)	(14,17)	(15,16)	(14,16)	(15,17)	(15,18)	(14,18)	(11,16)	(11,17)	(11,18)
"SCD"	(14,17)	5.9	-1.0																
	(15,16)	-1.0	5.9																
	(14,16)			6.5	.3														
	(15,17)			.3	6.5														
	(15,18)					8.1	0												
	(14,18)					0	8.1												
	(11,16)							10.2	0										
(11,17)							0	10.2											
(11,18)									12.3										
"TCD"	(14,17)	.05	0	-.6	.6						6.5	-.3							
	(15,16)	0	.05	.6	-.6						-.3	6.5							
	(14,16)	-.6	.6	.05	0								5.9	-.9					
	(15,17)	.6	-.6	0	.05								-.9	5.9					
	(15,18)					0	.5								8.1	0			
	(14,18)					.5	0								0	8.1			
	(11,16)							0	.5								10.2	0	
	(11,17)							.5	0								0	10.2	
	(11,18)									0									12.3

and B, respectively. The term in brackets is confined to atomic orbitals on the same center which was assumed ~ 1.2 eV. For the particular case of the $\phi_k e_{1u}(1s)$ orbital with π_{14} nodal character, $\pi_{14}(i)$ and $\pi_{15}(1)$, e.g.,

$$K_{i,j^*,j^*,i} \approx 1.04 \sum_A C_i C_i$$

$$= 0.601 \text{ eV}.$$

This value parallels the 0.6 eV which we conclude is indicative of this particular coupling from Fig. 1, i. e., $1/2\Delta E$ (satellites II and III) or $1/2\Delta E$ (satellites III and IV). In accord with these guidelines the interaction matrix to be diagonalized is given in Table VII. Our final results on benzene are tabulated in Table VIII and compared graphically with experiment in Fig. 3. Clearly, inclusion of the spin-symmetry breaking configurations and the accompanying near energetic degeneracy between the indicated levels leads to the observed number of features with correspondingly observed strengths at the approximate experimental energies.

IV. SUMMARY AND CONCLUSIONS

This study has demonstrated that the complex benzene core-hole excitation spectrum below 12.0 eV can be

TABLE VIII. The final-state benzene shake-up spectrum obtained by diagonalizing the matrix of Table VII. Experimental values are given in parentheses.

Energy (eV)	Intensity (%)	Parentage	Neutral
4.88 } (4.2)	0.00 } (<0.01)	${}^2B_{2u}^1$ ${}^2B_{1u}^3$	${}^1B_{2u}$ (4.80) ^a
4.98 }	<0.01 }		
5.27 (5.9)	3.74 (~2.0)	${}^2B_{1u}^1$ ${}^2B_{2u}^3$	${}^1B_{1u}$ (6.10) ^a
5.64	0.07	${}^2E_{1u}^1$ ${}^2E_{1u}^3$	
6.21	0.00	${}^2E_{1u}^3$	
6.81 (7.0)	6.14 (~6.0)	${}^2E_{1u}^1$	${}^1E_{1u}$ (6.79) ^a
7.74 (8.3)	2.26 (~2.0)	${}^2B_{1u}^1$ ${}^2B_{2u}^3$	
8.04	0.07	${}^2E_{1u}^1$ ${}^2E_{1u}^3$	
7.59	1.00	${}^2E_{2g}^1$ ${}^2E_{2g}^3$	${}^1E_{2g}$ (7.98) ^{a,b}
8.59 (9.0)	1.00 (≤ 1.0)		
9.70 } (10.7)	2.87 } (~3.0-4.0)	${}^2E_{2g}^1$ ${}^2E_{2g}^3$	${}^1E_{2g}$ (10.01) ^b
10.70 }	2.87 }		

^aSee, e.g., J. B. Birks, *Photophysics of Aromatic Molecules* (Wiley-Interscience, New York, 1970).

^bSee N. Nakashima, M. Sumitani, I. Ohmine, and K. Yoshihara, *J. Chem. Phys.* **72**, 2226 (1980); N. Nakashima, H. Inoue, M. Sumitani, and K. Yoshihara, *ibid.* **73**, 5976 (1980); and references contained therein.

elucidated in terms of *first-order* interactions modeled in accord with both a D_{6h} delocalized and C_{2v} symmetry-reduced equivalent-core solution. Although benzene presents particular computational difficulties because of the high spatial symmetry and consequent electronic degeneracies, the high symmetry also suggests certain relationships which allow the computation of the shake-up spectrum to be considerably simplified. Core-hole excitation energies were calculated to first-order based on well-defined approximations in terms of the neutral molecule, whereas intensities were obtained to first-order by projecting the C_{2v} localized core-hole solution from the delocalized description. Secondary first-order configuration interaction between doublet state manifolds was shown to yield the observed number of features with correspondingly observed intensities.

Particularly, our results indicate that the highly symmetric benzene structure leads to singlet- and triplet-coupled doublet states which are approximately energetically degenerate for excitations of specified orbital character causing significant secondary first-order configuration interaction between the doublet state manifolds. Also, we find that the relative contributions of the core-hole valence exchange terms to the shake-up energetics of the highly symmetric core-hole delocalized model allows an extraction of the appropriate doublet state energies directly from the neutral molecule problem. Theoretical intensities calculated within the sudden approximation yield a satellite spectrum in excellent accord with experiment. The total intensity contained in satellites I-IV was found to be largely attributable to a single $\pi^* \rightarrow \pi$ singlet-coupled doublet excitation, in terms of the localized description, which is distributed in apparent accord with experiment by symmetry-adapting the C_{2v} localized solutions to D_{6h} delocalized symmetry, and secondary configuration interaction between doublet state manifolds. Satellite V and the asymmetry on the high binding energy side of peak IV are assigned to $E_{2g}(\pi^* \rightarrow \pi)$ excitations on the basis of computed energies and intensities. The assignment of these higher-lying features as ${}^1E_{2g}(\pi^* \rightarrow \pi)$ in *origin* provides further conformation for the numerous theoretical predictions and recent conclusions based on spectroscopic investigation for states of E_{2g} symmetry at approximately 8.0 and 10.0 eV in neutral benzene (see the footnotes to Table VIII).

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²⁷Alternatively, the core hole or second excitation plus core hole can be viewed as a symmetry breaking operator $\Theta(\phi_h, \psi_{ij}^i(k), \psi_{ij}^{i'}(k), \psi_{ij}^{i''}(k), \dots)$ connecting the initial (*I*) and final (*F*) states $\langle F | \Theta | I \rangle$ such that $\Gamma_F \otimes \Gamma_\Theta \otimes \Gamma_I \subset A_{1g}$.

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- ³⁵Subject to the stated approximations ${}^2\tilde{E}_{ij'}^1(k) > {}^2\tilde{E}_{ij'}^1(k)$ “level reversal” is expected for $\pi^* \leftarrow \sigma$ or $\sigma^* \leftarrow \pi$ excitations since $K_{\sigma\sigma^*} \ll K_{\pi\pi^*}$ and $K_{\sigma\sigma^*}$. These types of excitations, however, do not enter into our interpretation of the low-energy shake-up spectrum.
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