Analysis on Excitation of Molecules with I_h Symmetry: Frozen Orbital Analysis and General Rules

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A frozen-orbital analysis (FZOA) that has been proposed in order to analyze excitation between degenerate orbitals is applied to molecules with I_h symmetry such as $(B_{12}H_{12})^{2-}$ and C_{60}. In the FZOA approach, the ordering and the energy splittings of the excited states involving degenerate orbitals can be understood through a simple and intuitive picture. FZOA results for molecules with I_h symmetry also reveal that two general rules hold: (i) The highest transition among transitions between degenerate orbitals is dipole-allowed; (ii) The excitation energy of the highest transition is larger than those of the other transitions.

Excitation from molecules with I_h symmetry has attracted much attention in connection with functional materials such as $(B_{12}H_{12})^{2-}$ and C_{60}, which are capable of encapsulating other elements. These high-symmetry molecules exhibit peculiar characters such as excited spectra splitting and dipole-allowed and forbidden transitions. Since a molecule with high symmetry has many degenerate orbitals, the degenerate excited states consist of excitation among degenerate orbitals. Theoretical research on such excited states has mainly focused on assignments of excitation spectra. However, no analysis techniques and chemically intuitive concepts on this topic have been put forth.

We have proposed a frozen-orbital analysis (FZOA)[1] in order to understand the nature and the ordering of the excited states. FZOA is capable of analyzing general characteristics about excitation between degenerate orbitals since FZOA takes into account singly excited states within the active space consisting of only degenerate orbitals. So far, we have applied FZOA to several molecules and obtained the following simple and clear general rules: (i) The highest transition among transitions between degenerate orbitals is dipole-allowed; (ii) The excitation energy of the highest transition is larger than those of the other transitions.

In this paper, we investigate excitation of I_h symmetry molecules such as $(B_{12}H_{12})^{2-}$ and C_{60}, which possess the potential to exhibit new properties. The molecular excitation energies among degenerate orbitals are analyzed by FZOA. One- and two-electron integrals are computed by the modified GAMESS program,[2] and FZOA excitation energies are calculated by the original program. The cc-pVDZ[3] and 6-31G[4] basis sets are adopted for $(B_{12}H_{12})^{2-}$ and C_{60}. The B–B and B–H bond distances are optimized to be 1.821 and 1.194 Å by the Hartree–Fock (HF) method. The bond distance of C–C in C_{60} is 1.42 Å. The SAC-CI[5] calculations are also performed for comparison. For analysis, I_h symmetry is lowered to D_{2h} symmetry for both $(B_{12}H_{12})^{2-}$ and C_{60} molecules.

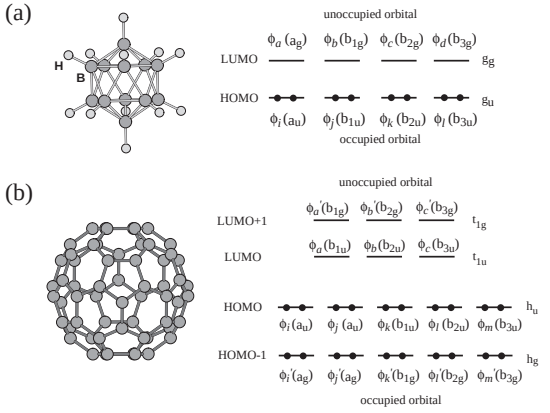

Figure 1. Structures and molecular orbitals of $B_{12}H_{12}{}^{2-}$ and C_{60}.

We first investigate excitation of $(B_{12}H_{12})^{2-}$ in which both the highest occupied molecular orbital (HOMO) and lowest unoccupied MO (LUMO) are fourfold, as shown in Figure 1a. The degenerate occupied and unoccupied MOs have g_u and g_g symmetry in I_h point group. The FZOA corresponds to configuration interaction singles (CIS) within the minimal active space, which consists of the highest occupied g_u and the lowest unoccupied g_g orbitals. The excitation energies in FZOA, which are determined only by the symmetry rule, are decomposed into three terms: $\Delta E = A + B + C$. A is the orbital energy difference $\Delta\varepsilon$, B is the $(-J_{ov} + 2K_{ov})$ type, and C is the $(oo'|vv')$ and $(ov|o'v')$ type terms. J_{ov} and K_{ov} represent $(oo|vv)$ and $(ov|ov)$, respectively. The indexes $\{o,o'\}$ and $\{v,v'\}$ represent general occupied and virtual orbitals. B and C terms originate in diagonal and off-diagonal elements of Slater determinant-based CIS, respectively. Explicit expressions of the A, B, and C terms are listed in Table 1.

Figure 2 illustrates the energy splitting of the five singlet excited states, T_{1u}, T_{2u}, G_u, H_u, and A_u. The energy levels in the left are estimated by A terms, the orbital energy differences $\Delta\varepsilon$. The approximately two energy levels whose gap is about 1.0 eV are obtained by considering not only A but also B terms. The five energy levels on the right-hand side are reproduced by $A + B + C$ terms. The large gap between T_{1u} and other states are enhanced

Table 1. FZOA energy components of HOMO → LUMO excitation energies for $(B_{12}H_{12})^{2-}$

State	A	B	C
A_u	$\Delta\varepsilon$	$1/4(-J_{ia} + 2K_{ia}) + 3/4(-J_{jb} + 2K_{jb})$	$3/2\{-(ij\|ab) + 2(ia\|bj)\} + 3/2\{-(jk\|cb) + 2(jc\|bk)\}$
T_{1u}	$\Delta\varepsilon$	$1/2(-J_{ib} + 2K_{ib}) + 1/2(-J_{kd} + 2K_{kd})$	$1/2\{-(ij\|ab) + 2(ib\|aj)\} + 1/2\{-(jk\|cb) + 2(jb\|ck)\} + \{-(ik\|db) + 2(ib\|dk)\} + \{-(jk\|da) + 2(ja\|dk)\}$
T_{2u}	$\Delta\varepsilon$	$1/2(-J_{ib} + 2K_{ib}) + 1/2(-J_{kd} + 2K_{kd})$	$1/2\{-(ij\|ab) + 2(ib\|aj)\} + 1/2\{-(jk\|cb) + 2(jb\|ck)\} - \{-(ik\|db) + 2(ib\|dk)\} - \{-(jk\|da) + 2(ja\|dk)\}$
G_u	$\Delta\varepsilon$	$3/4(-J_{ia} + 2K_{ia}) + 1/4(-J_{jb} + 2K_{jb})$	$-3/2\{-(ij\|ab) + 2(ia\|bj)\} + 1/2\{-(jk\|cb) + 2(jc\|bk)\}$
H_u	$\Delta\varepsilon$	$(-J_{jb} + 2K_{jb})$	$\{-(jk\|cb) + 2(jc\|bk)\}$

Table 2. FZOA and SAC-CI excitation energies and energy components of FZOA excitation energies for $(B_{12}H_{12})^{2-}$ in eV

State	FZOA								SAC-CI
	A Term	*B* Term			*C* Term			Transition dipole	Excitation energy $(A+B+C)$	
	$\Delta\varepsilon$	J_{ov}	K_{ov}	Total $(-J+2K)$	$(oo'\|vv')$	$(ov\|o'v')$	Total			
T_{1u}		5.79	0.60	−4.59	−0.03	1.13	2.29	1.27	12.06	9.76
T_{2u}					−0.03	−0.26	−0.49	0.00	9.26	8.79
G_u	14.41	5.70	0.14	−5.41	−0.01	0.07	0.14	0.00	9.15	8.53
H_u		5.76	0.10	−5.56	0.06	0.23	−0.01	0.00	8.84	8.43
A_u		5.74	0.12	−5.51	−0.10	−0.12	−0.13	0.00	8.77	8.27

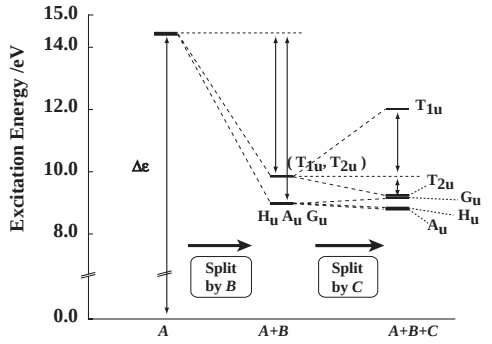

Figure 2. Schematic picture of excitation-energy splitting of $(B_{12}H_{12})^{2-}$.

by the *C* term, while energy differences among other states of T_{2u}, G_u, H_u, and A_u are less affected.

Let us examine more details. Table 2 lists the estimated values of *A*, *B*, and *C* of five distinct excited states. The value of the *A* term is exactly the same for all states because of the degeneracy. As regards the *B* term, the J_{ov} integrals of the *B* term range 5.70–5.79 eV, while K_{ov} exhibits a strong dependence on kind of states: 0.60 eV for T_{1u} and T_{2u} states and 0.10–0.14 eV for G_u, H_u, and A_u states. This is attributed to the fact that exchange-type integrals strongly depend on orbital-overlap variations. After the consideration of the *B* terms, two degenerate states (T_{1u} and T_{2u}) and three quasi-degenerate states (G_u, H_u, and A_u) are obtained. As regards the *C* term, $(ov|o'v')$ are large contributions: 1.13 eV for T_{1u} and −0.26 eV for T_{2u}. Thus, T_{1u} and T_{2u} are considerably split by *C* terms. This means that the interaction between different singly excited states is important. On the other hand, the three quasi-degenerate states (G_u, H_u, and A_u) vary less significantly. $(oo'|vv')$ makes relatively smaller contributions than $(ov|o'v')$. From transition moments estimated by FZOA wavefunctions, only the T_{1u} state is a dipole-allowed transition, and the other states are not. This is consistent with the previous results.[1] The excitation energy of the dipole-allowed T_{1u} state by the FZOA method is calculated to be 12.06 eV, which is larger than 9.76 eV for the SAC-CI method. This overestimation is ascribed to the limitation of the excitation space. The other states range from 8.77 to 9.26 eV, which are relatively close to those of SAC-CI. Since the order of excited states and the large gap between the dipole-allowed T_{1u} state and the other states are qualitatively reproduced by FZOA calculations, FZOA results are reliable.

As shown in Figure 1b, the C_{60} molecule has fivefold degenerate next HOMO (HOMO–1), fivefold degenerate HOMO, three-fold degenerate LUMO, and threefold degenerate next LUMO (LUMO+1), which correspond to h_g, h_u, t_{1u}, and t_{1g} symmetries in I_h point group, respectively. Although four combinations of single excitation are considered in FZOA calculations, only the transitions to singlet T_{1u} states appearing in HOMO → LUMO+1 and HOMO–1 → LUMO excitation are dipole-allowed. Thus, we focus on HOMO → LUMO+1 and HOMO–1 → LUMO. Table 3 summarizes the excitation energies of the four distinct excited states T_{1u}, T_{2u}, G_u, and H_u from the ground state in C_{60} calculated by FZOA. We examine the general rules for HOMO–1 → LUMO and HOMO → LUMO+1. The highest excitation is a dipole-allowed transition to T_{1u} state for both cases. The large gap between the T_{1u} state and other states are also observed: 1.39 eV for HOMO–1 → LUMO and 0.80 eV for HOMO → LUMO+1. A similar analysis has been carried out by another group.[6]

Table 3. Excitation energies of C_{60} by FZOA in eV

	Excitation energy	Transition dipole	Excitation energy	Transition dipole
	HOMO–1 → LUMO		HOMO → LUMO+1	
T_{1u}	5.43	4.92	4.94	2.91
G_u	4.04	0.00	4.04	0.00
H_u	4.03	0.00	3.99	0.00
T_{2u}	3.99	0.00	4.14	0.00

In conclusion, we have analyzed the I_h symmetry molecules such as $(B_{12}H_{12})^{2-}$ and C_{60} using the FZOA technique. The splitting is understood in terms of the two-electron integrals, namely, the *B* and *C* terms. We also confirm that (i) The highest transition is dipole-allowed; (ii) The highest transition has a larger energy gap. This analysis leads to the conclusion that the ordering of transitions between degenerate orbitals is mainly determined by symmetry, not the constituent atoms.

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