

CLUSTER EXPANSION OF THE WAVEFUNCTION: IONIZATIONS AND SOME LOW-ENERGY EXCITATIONS OF NAPHTHALENE

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Ionizations and some lower singlet valence and Rydberg excitations of naphthalene are studied by the SAC/SAC CI method with 100 (44 π + 56 σ) active MOs. A systematic assignment of the ionization spectra is given. In particular, assignments are given for the peaks in the 13–20 eV region. A large σ -electron correlation effect is found for the valence excited B_{1u} state, together with a large effect of the d_{π} polarization function. The controversy concerning the assignment of the Rydberg nd_{π} orbitals is resolved: Robin's assignment of the $3d_{\pi}$ orbital at 6.73 eV above the ground state is supported.

1. Introduction

In this series of articles [1–13], we have developed SAC (symmetry adapted cluster) and SAC CI theories and applied them to molecular excited and ionized states. In particular, we have been interested in electron correlation in the excited and ionized states of conjugated π -electron systems. We have applied SAC/SAC CI methods to formaldehyde [7], ethylene [8], five-membered rings (cyclopentadiene, pyrrole and furan) [9], benzene [10], and pyridine [11]. Through these studies we have been able to elucidate some important features of electron correlation in excited states, in particular on the role of σ -electron correlation in valence π - π^* excitations [7–11]. Utilizing our previous experience we have undertaken a study of naphthalene.

There have been several previous studies of the excited states of naphthalene. Platt and Kleven's [14] were the first to observe the UV spectrum and more recently, the EELS [15] and TPS [16] spectra were reported. Many semi-empirical calculations [17] using the PPP and the CNDO/S method have been carried out to give an assignment for the observed spectra. However, ab initio calculations have been very limited; to the best of our knowledge there is only one ab initio CI calculation on the triplet excitation by Ha and Wild [18].

In this paper we present preliminary results on the

ionizations and excitations of naphthalene. We discuss in particular the following three points:

(1) A systematic assignment of the ionization spectra including the first assignment for the 13 to 20 eV region.

(2) The effect of σ -electron correlation on the valence π - π^* excitations.

(3) The discrepancy between the assignments of Robin [19] and Angus et al. [20,21] for the singlet Rydberg nd_{π} excitations.

2. Computational method

We use the following two kinds of basis sets (V and R sets). For both basis sets we employ the [3s2p/2s] set of Huzinaga and Dunning [22] and Rydberg p_{π} functions (0.03477, 0.01075) on each carbon atom. In the R set, Rydberg s (0.0437, 0.0184), p (0.0399, 0.0168) and d (0.0285, 0.01075) functions are placed at the center of the molecule, and in the V set a d_{π} polarization function (0.75) is placed on each carbon atom. The number of atomic orbitals is 146 for both basis sets. The active spaces consisting of all π MOs (44 for the R and 58 for the V set) and $\pi + \sigma$ MOs (44 π + 56 σ for both sets) are used. The geometry is fixed at the experimental values for the ground state [23]. The dimensions of the matrices to be solved in the SAC/SAC CI method are

reduced by the configuration selection technique [5] with thresholds of 10^{-5} au for the π space and 10^{-5} – 4.0×10^{-5} au for the $\pi + \sigma$ space. The maximum dimensions are about 6500 for the singlet states and about 2400 for the ionized states. These dimensions are relatively small, in comparison with ordinary CI methods, by virtue of the SAC/SAC CI formalism [1–4]. For the ionized states, we can diagonalize the matrices directly by the Householder-bisection method, so we can easily calculate shake-up peaks. The unlinked terms in the SAC and SAC CI wavefunctions are calculated only for those excitation operators whose coefficients in the SDCI for the ground state are larger than 10^{-2} and 10^{-3} , respectively.

3. Results and discussion

3.1. Ground state

Table 1 shows the energy of the ground state of naphthalene calculated by the SAC method. The correlation energy calculated using the $\pi + \sigma$ active space is more than twice as large as that obtained with the π space alone, though the inclusion of the unlinked contribution is limited in this calculation. We note that the d_π polarization functions included in the V set are very effective.

3.2. Ionization potential

We display the ionization potentials calculated by the SAC CI and Koopmans methods together with the experimental values [24] in table 2. Although

the ordering of the states is the same between the Koopmans and SAC CI results, the latter gives better agreement with experiment, especially in the higher energy region. The average deviation from those existing experimental values less than 13 eV is 1.31 eV for Koopmans' method, 0.21 eV for the π SAC CI method, and 0.28 eV for the $\pi + \sigma$ SAC CI method.

We compare the experimental [24] with the theoretical spectrum in fig. 1. The peak intensities were calculated using the monopole approximation [25]. Although Brundle et al. assigned only peaks lower than 13 eV, the peaks in the 13–20 eV region are assigned here for the first time based on the SAC CI results. Table 2 includes the present assignment in the 13–17 eV region. There are four or five peaks in the theoretical spectrum between 13 and 15 eV, and two peaks between 15 and 17 eV. The experimental peak at 16.0 eV may be assigned either to the theoretical peak at 15.1 eV or to the small shake-up peak at 16.0 eV. In the latter assignment, the theoretical peak at 15.1 eV would be assigned to the shoulder at 14.8 eV in the experimental spectrum. The difficulty in the latter assignment is the small value of the calculated intensity for the shake-up peak, though generally speaking, the intensity of shake-up peaks calculated by the SAC CI method with the monopole approximation is less than experiment [5]. The average discrepancy for the peaks assigned here is 0.28 eV for the former assignment and 0.16 eV for the latter. Further, we can explain the comparatively weak and broad experimental peak at 17.5–20 eV as a composite of shake-up peaks having B_{1g} , B_{3u} , and B_{2u} symmetries. These peaks borrow their intensities from the 1π , 2π and 27σ MOs, respectively.

Table 1
Total energy and correlation energy of the ground state of naphthalene ^{a)} (au)

	R basis set	V basis set
Hartree-Fock	–383.24701 (0.0)	–383.27598 (0.0)
π space		
SD CI	–383.36149 (–0.11449)	–383.39626 (–0.12028)
SAC	–383.37032 (–0.12331)	–383.40294 (–0.12696)
$\pi + \sigma$ space		
SD CI	–383.49457 (–0.24756)	–383.54343 (–0.26744)
SAC	–383.49796 (–0.25095)	–383.54626 (–0.27027)

^{a)} Values in parentheses show the correlation energy.

Table 2
Ionization potentials of naphthalene (eV) ^{a,b)}

MO	Koopmans	π SAC CI	44 π + 56 σ SAC CI	Exptl. ^{c)}	
				BRK ^{c)}	present assignment ^{d)}
5 π a _u	8.12	8.01 (-0.12)	7.68 (-0.45)	8.13	
4 π b _{3u}	8.86	8.57 (-0.31)	8.22 (-0.66)	8.88	
3 π b _{2g}	10.63	10.01 (0.00)	9.75 (-0.26)	10.01	
2 π b _{1g}	12.38	11.22 (0.32)	10.94 (0.04)	10.90	
29 σ a _g	13.02		10.97 (-0.11)	11.08	
28 σ b _{3g}	13.15		11.06 (-0.31)	11.37	
27 σ b _{2u}	14.32		12.22 (0.33)	11.89	
1 π b _{3u}	14.70	12.80 (0.30)	12.59 (0.09)	12.50	
26 σ b _{1u}	15.54		13.38 [-0.1]		13.5
25 σ b _{2u}	15.89		13.47 [-0.3]		13.8
24 σ b _{3g}	16.09		13.98 [-0.2]		14.2
23 σ a _g	16.85		14.47 [0.0]		14.5
22 σ b _{1u}	17.12		15.10 [-0.9,03]		16.0,14.8 ^{e)}
shake-up	-		16.00 [0.0]		16.0 ^{e)}
21 σ a _g	18.54		16.69 [0.2]		16.5
average deviation	1.31	0.21	0.28, 0.22		

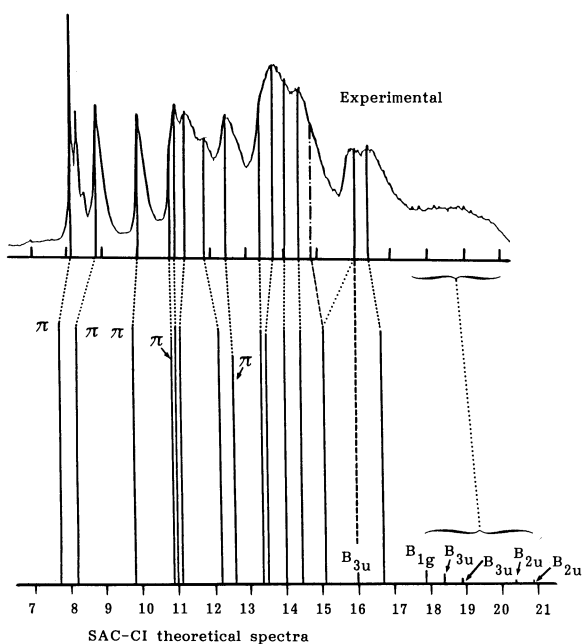
^{a)} Results using basis set V.

^{b)} Values in parentheses show deviations from the experimental values.

^{c)} Ref. [24].

^{d)} Peak maxima of the experimental spectrum of Brundle et al. are assigned using the present SAC CI calculations.

^{e)} For this assignment, see text.



3.3. Singlet excitation

For the valence excitations, the lowest two states having B_{2u} and B_{1u} symmetries are computed by the SAC CI method and the results are summarized in fig. 2. Inclusion of both the d_π polarization functions and the σ orbitals in the active space has no effect on the B_{2u} state. The discrepancy is 0.79 eV. On the other hand, for the B_{1u} state, the excitation energy is lowered by 0.35 eV on inclusion of the d_π polarization functions and by a further 0.62 eV by including σ orbitals in the active space. The total improvement is 0.97 eV. The discrepancy from the experimental value [16,26] is 0.62 eV. Further attempts to improve on these states and calculations

◀ Fig. 1. Experimental (above) and theoretical (below) ionization spectra of naphthalene. The correspondence between these peaks shows the assignment. Two different assignments are given for the experimental peaks at 14.8 and 16.0 eV. See text for the details. The experimental spectrum is due to Brundle et al. [24].

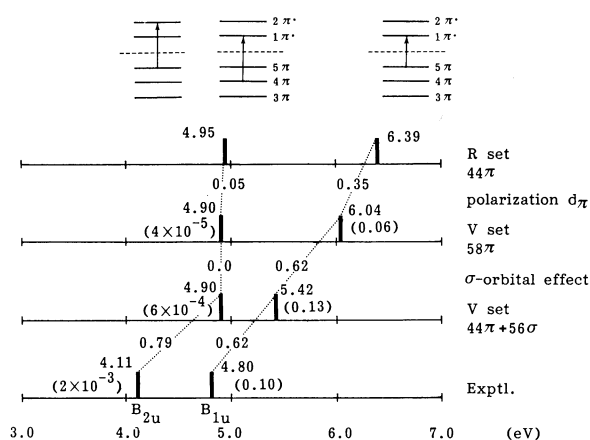


Fig. 2. Comparison of the theoretical and experimental excitation energy for the lower two singlet valence excitations of naphthalene (eV). The values in parentheses show oscillator strengths. The experimental values are due to ref. [16].

for other excited states are currently undertaken. Fig. 2 also shows the oscillator strengths (in parentheses). The σ orbital effect is relatively large. Values calculated with the $\pi + \sigma$ space agree well with experiment [16].

For the Rydberg excited states, we have obtained excitation energies from the 5π orbital to the $3p_\pi$ and $3d_\pi$ orbitals, and the results are shown in fig. 3. The effect of the σ orbitals in the active space is about

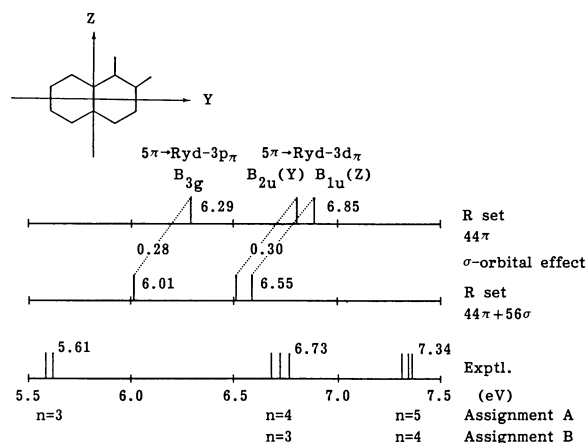


Fig. 3. Comparison of the theoretical result for the $5\pi \rightarrow 3p_\pi$ and $3d_\pi$ Rydberg transitions with the two experimental assignments (A and B) due to Angus et al. [20,21] and Robin [19], respectively.

0.3 eV, nearly one half of that for the valence B_{1u} state. There is a controversial assignment of the Rydberg d_π transition: Angus et al. [20,21] assigned $3d_\pi$ to the peak at 5.6 eV and $4d_\pi$ to that at 6.7 eV, but Robin [19] assigned the peaks at 6.7 eV as the transition to the $3d_\pi$ orbital. The present SAC CI result supports Robin's assignment (assignment B in fig. 3). The deviation from the experimental value is 0.18 eV. The peaks at 5.61 eV may then be assigned to either the forbidden $5\pi \rightarrow 3s$ or $3p$ transitions [19] or to hot bands of the adjacent $\pi \rightarrow \pi^*$ excitation [27]. The present SAC CI value for the $5\pi \rightarrow 3p_\pi$ transition is 6.01 eV.

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