Theor Chim Acta (1988) 74: 363-379

Theoretica Chimica Acta

A CASSCF study of the singlet–singlet and triplet–triplet spectroscopy of naphthalene

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(Received January 18; revised and accepted April 12, 1988)

Ab initio complete active space (CAS) SCF calculations have been carried out for the singlet and triplet excited states of naphthalene molecule. The CASSCF active space comprised 10 π-type molecular orbitals. The basis set was of ANO type and included both diffuse functions and polarization functions. The calculated excitation energies and transition moment provide a sound theoretical basis for the assignment of the experimental singlet-singlet and triplet-triplet spectra of the naphthalene molecule.

Key words: CASSCF — Naphthalene — Spectrum — Transition moments — Quadrupole moments

1. Introduction

The naphthalene molecule, due its lower symmetry (D_{2h}) presents a rich absorption spectrum with a number of allowed transitions that are forbidden in benzene, the standard aromatic molecule. Therefore it has been extensively studied experimentally [1-17] and several semiempirical calculations have been performed as attempts to assign the various singlet-singlet (S-S) and (T-T) transitions [18-24].

Most of the experimental studies have been performed in solution or in the solid phase, and the effect of the environment often precludes the assignment of the transitions. The spectra contain wide overlapping bands with intensity borrowing due to vibronic interactions. A few gas phase experiments exist [6, 14, 16], but the complexity of the spectra also make definitive assignments difficult. The

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results of the semiempirical calculations are often conflicting and even the ordering of the lower states is not well established [13]. The difficulties arise mainly from the necessity to include multiply excited configurations into the wave function, which cannot be done in a consistent way in the parametrized Pariser-Parr-Pople (PPP) method. The importance of these multiply excited π-electron configurations is clearly illustrated in the present work.

The size of the naphthalene molecule has hitherto prevented any large scale *ab initio* studies of its electronic spectrum. SCF (self consistent field) calculations have been reported for the ground state [25-27], the anion, cation, and for the first triplet state [28]. The T-T spectrum has been studied by Ha and Wild [29] using a restricted singles and doubles configuration interaction (SDCI) wave function with an STO-3G basis set. This study is, however, too limited to be useful for assigning the spectrum. A more extended SAC CI study of the ionization energies and the two lowest singlet excited states has recently been reported by Nakatsuji et al. [30]. However, no *ab initio* calculation has so far been performed which gives a complete theoretical description of the valence excited spectrum of the naphthalene molecule.

The present authors have recently published a complete active space (CAS) SCF and multireference CI study of the electronic spectrum of benzene [31]. It was shown that large basis sets and inclusion of diffuse functions and polarization functions were needed in order to reproduce excitation energies with an accuracy of $\simeq$0.5 eV. For excited states with large ionic character in the wave function, σ-π correlation also had to be included in order to achieve this accuracy. The error obtained when only the π-electrons were correlated was in some cases as large as 1.0-2.0 eV.

A calculation at the same level of theory cannot be performed today for the naphthalene molecule, which has 48 valence electrons. However, directed by the experience achieved in the study of benzene, and motivated by the lack of *ab initio* results for naphthalene it was decided to carry out a CASSCF study of the ground state and valence excited states of naphthalene. It can be expected that such a calculation gives too large excitation energies for some of the excited states, but an assignment of the S-S and T-T spectra ought to be possible by the combined use of energies and transition moments. The latter were less affected by σ-π correlation and were for the benzene molecule well reproduced at the CASSCF level of theory.

The results of the study are reported in the present communication. A CGTO basis set including d-type polarization functions was used and the active space comprised the 10 π-electrons distributed in 10 π-orbitals. Calculated excitation energies for the first excited singlet and triplet states are in good agreement with experimental data, while the higher excitations, as expected, show larger errors. Computed transition moments are in all cases in agreement with measurements, which is in line with our earlier experience from the study of the benzene molecule. Based on the calculated energies and transition moments, a consistent assignment is made of both S-S and T-T spectra. In addition we have computed the quadrupole moment for each electronic state. The computed value for the ground state agrees well with experiment, giving further confidence to the electron distribution computed in this study.

2. Details of the calculation

2.1. The basis set

The molecular geometry assumed in all calculations was that observed experimentally by Innes et al. [32], with the point group D_{2h}. In the calculations the molecule has been placed in the *xy* plane with the long molecular axis corresponding to the *x*-axis.

Contracted Gaussian type functions of the ANO type [33] were used as atomic basis functions. Starting from the C (10*s*, 6*s*) and H (6*s*) basis set of Duijneveldt [34], the carbon primitive set was augmented with two diffuse *s*-type and two diffuse *p*-type functions, and also one *d*-type polarization function. The *d*-type function was the same as had been used in the earlier calculations on benzene (exp = 0.63) [31]. The contraction scheme used [35] is a modified version of the atomic natural orbital method (ANO) proposed by Almlöf and Taylor [33]. Each basis function is in this scheme obtained as a linear combination of all primitives of a given type. The ANO basis sets has proven to be superior to all segmented basis sets used earlier. The expansion coefficients for the ANO's were obtained from large active space CASSCF calculations on $C^+(^2P)$, $C(^3P)$, $C^-(^2P)$ for carbon and on H_2 for hydrogen [36]. The final ANO basis set is given in Table 1.

CASSCF calculations were performed on the benzene molecule in order to test the quality of the basis set. With the same active space as used previously for benzene [31], calculations were performed for the ground state, the $^1B_{2u}$ valence excited state and the $^1E_{1u}$ Rydberg state. The computed ground state energy was −230.8293 au to be compared with −230.8133 au obtained with a segmented basis set of similar size [31]. The computed excitation energies for the two excited states were 4.9 and 6.8 eV, respectively, which compares well with the values 4.9 and 6.8 eV obtained in the earlier study [31].

The ANO basis set used for naphthalene comprises 196 contracted basis functions. The SCF energy obtained with this basis set is given in Table 2, where it is compared with previous SCF results. It would have been desirable to increase the basis set even more, e.g. by adding more diffuse *p*-type functions, but the size of the system prevents further extension. The tests on benzene give some confidence that the basis set should be adequate for a description of the valence excited states of naphthalene.

Surprisingly enough our SCF energy for naphthalene is not as low as the value reported by Nakatsuji et al. [30] (cf. Table 2). Their basis set is based on a smaller set of primitives and is of the segmented type. The contraction is $(3s2p/2s)$ while the present ANO is $(3s3p/2s)$. In addition they add two Rydberg p_π functions to the basis set, but it is unlikely that those functions could balance the use of

Table 1. Generalized contracted Gaussian functions for naphthalene ground and excited states calculations

Carbon exponent	Coefficient		
	1*s*	2*s*	3*s*
880 6.6534	0.0004889	−0.0001073	0.0000062
131 9.2820	0.0037877	−0.0008302	0.0000736
29 9.51876	0.0195245	−0.0043331	0.0001862
8 4.338836	0.0765722	−0.0173276	0.0018264
2 7.133675	0.2237136	−0.0546747	0.0011529
9.493353	0.4286758	−0.1253907	0.0185245
3.486330	0.3623315	−0.1829973	−0.0128572
1.017479	0.0470939	0.1094432	0.0925582
0.393724	−0.0097356	0.6346125	−0.3796239
0.134271	0.0044315	0.3781935	0.8289354
0.046	−0.0018640	0.0146694	−1.8054260
0.016	0.0056980	0.0059424	1.9296820
	2*p*	3*p*	4*p*
3 2.692100	0.0058869	−0.0019638	0.0053208
7.472610	0.0391495	−0.0135500	0.0323481
2.239240	0.1509879	−0.0504712	0.1414525
0.772810	0.3610067	−0.1668447	0.4597589
0.274840	0.4412629	−0.0620588	0.0848386
0.095840	0.2186017	0.1058422	−0.7148962
0.033	0.0454370	−0.0384028	−0.5110609
0.012	0.0224278	0.9794692	0.7113560
	3*d*		
0.63	1.000		
Hydrogen	1*s*	2*s*	
8 2.636374	0.0020063	0.0072163	
1 2.409558	0.0153451	0.0512978	
2.8238540	0.0755770	0.2556738	
0.7976700	0.2569216	0.7439769	
0.2580530	0.4973803	−0.0690643	
0.0898910	0.2960691	−0.8576619	

a full third set of *p*-type functions. At present we therefore have no explanation for the discrepancy between the two calculations.

2.2. *CASSCF calculations*

All calculations presented in this work have been done using the complete active space (CAS) SCF method [37–39]. It is a well established method having the advantage of including the most important correlation effects together with an optimization of all orbitals. The orbitals in the CASSCF method are split into an inactive and an active part, where the inactive orbitals are doubly occupied

Table 2. Naphthalene ground state SCF total energies in atomic units

E_{SCF}						
[30][a]	This work	[28][b]	[25][c]	[27][d]	[29][e]	[26][f]
−383.2760	−383.2526	−383.2142	−382.7883	−382.3713	−378.6822	−328.1097

[a] $(3s2p/2s)$ basis set of Huzinaga and Dunning augmented with two p_π-type functions and one d_π-type function for the carbon atoms

[b] Gaussian basis functions, C$(10s, 5p/4s, 2p)$, H$(4s/2s)$

[c] 10 single Gaussians expanding the carbon s atomic orbitals, 5 Gaussian lobe functions to represent the carbon $2p$ orbitals and 5 Gaussians for the expansion of $1s$ hydrogen orbital, C$(3s/1p)$, H$(1s)$

[d] Gaussian basis functions, C$(7s, 3p/2s, 1p)$, H$(3s/1s)$

[e] STO-3G basis set

[f] Floating spherical Gaussian orbitals

in all configurations state functions (CSF's). The CAS wave function comprises all CSF's which can be formed by distributing the remaining electrons among the active orbitals in all possible ways with a given overall spin and space symmetry.

The active orbital space chosen for naphthalene comprised the 10 π-orbitals in the system. Thus the wave function contains all CSF's corresponding to excitations within the valence π-orbitals. In the previous study of benzene [31] twelve active π-orbitals were used to describe the wave function for the six π-electrons. The present calculation is more approximate, since it does not allow for the radial correlation effects induced by the second π-orbital shell. Such a CASSCF calculation is not possible for naphthalene. In benzene CI calculations were performed in order to include σ-π correlation. This had a substantial effect on calculated excitation energies, in some cases leading to a decrease of almost 1.0 eV. Such calculations have not been undertaken here due to the larger size of the molecule. Guided by the experience gained in the benzene study we expect errors of the order of 0.0–2.0 eV for calculated excitations energies in naphthalene. Even if these errors are rather large, an assignment of the electronic spectra will still be possible by the combined use of calculated energies and transition moments.

CASSCF wave functions were in some cases obtained for states, which are not the lowest of a given symmetry. Orthogonality between different states having the same symmetry is not guaranteed in this computational scheme. Checks of the overlap integral showed, however, that the overlap was less than 0.01 in all cases.

The transition moments are expected to be reasonably well predicted at the CASSCF level of theory. They are computed using a method developed by Malmqvist [40], which is based on non-unitary transformations of the inactive and active orbitals. The quadrupole moment of each state has been computed as the average value of the corresponding operator.

Table 3. Direct product of the irreducible representations of the π orbitals of naphthalene

D_{2h}	A_u	B_{1u}	B_{3g}	B_{2g}	B_{1u}
A_u	A_g				
B_{1u}	B_{1g}	A_g			
B_{3g}	B_{3u}	B_{2u}	A_g		
B_{2g}	B_{2u}	B_{3u}	B_{1g}	A_g	
B_{1u}	B_{1g}	A_g	B_{2u}	B_{3u}	A_g

Table 4. Number of CSF's in the CAS wave function for different states of naphthalene

State	Singlets	Triplets
A_g	4936	7360
B_{1g}	4816	7440
B_{2u}	4836	7460
B_{3u}	4816	7440

3. Results

3.1. *The singlet states*

The direct products of the irreducible representations of the π-orbitals of D_{2h} naphthalene are shown in Table 3, thus defining the possible symmetries of the states arising from excitations among these orbitals. The closed shell ground state is of A_g symmetry and singly excited states have the symmetries A_g, B_{1g}, B_{2u}, and B_{3u}. The number of CSF's in the CAS wave functions for the different excited states is given in Table 4.

The CASSCF energy for the ground state was computed to be −383.3730 au, which compares well with the SAC (π) energy, −383.4029 au recently reported by Nakatsuji et al. [30]. The π-electrons were in their study correlated using an orbital space consisting of 58 MO's.

Details of the electronic structures for the ground and excited states are presented in Tables 5 and 6. Table 5 gives the total energies, the weight of the most important configurations and the number and weights of singly (S), doubly (D) and triply (T) excited configurations with CI coefficients larger than 0.05. The natural orbital occupation numbers and the $\langle z^2 \rangle$ expectation values for the active orbitals are shown in Table 6.

The quadrupole moments have been computed for all the states. The results are presented in Table 7. The calculated value of the out-of-plane component for the ground state is −8.4 au, to be compared with an experimental value of −10.0±1.1 [41]. An earlier SCF calculation of Chablo et al. [42] in a DZ basis gave the value −10.9 au. They obtained a value of 1.123 for the ratio between the in-plane components. The corresponding value obtained here is much larger: $Q_{yy}/Q_{xx}=3.805$.

CASSCF calculations were performed for eight singlet excited states corresponding to the two lowest states of symmetries A_g, B_{1g}, B_{2u}, and B_{3u}. The computed excitation energies, transition moments, and oscillator strengths are given in Table 8.

The first excited singlet state is of B_{3u} symmetry, with the polarization along the x-axis (the long molecular axis). The vertical excitation energy (4.5 eV) agrees well with the value 4.0 eV observed in the gas phase energy-loss spectrum [16]. A naphthalene vapor absorption spectrum yields the value 32 020 cm^{-1} (3.97 eV)

Table 5. Naphthalene ground and excited states: principal configurations and weights, total energies, number and (weights) of singly, doubly, triply excited configurations with coefficients larger than 0.05

State	Principal configurations	Weight				
		(%)	E_T (au)	S	D	T
$1\,^1A_g$	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^2(1a_u)^2$	82	−383.37304		13 (13%)	
$1\,^1B_{3u}$	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^2(1a_u)^1(2b_{3g})^1$	34	−383.20742	4 (76%)	21 (14%)	3 (1%)
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^1(1a_u)^2(2b_{2g})^1$	38				
$2\,^1A_g$	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^1(1a_u)^2(3b_{1u})^1$	31	−383.15288	4 (62%)	21 (19%)	4 (2%)
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^1(2b_{1u})^2(1a_u)^2(2b_{3g})^1$	27				
$1\,^1B_{2u}$	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^2(1a_u)^1(2b_{2g})^1$	77	−383.12565	2 (86%)	9 (4%)	2 (1%)
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^1(1a_u)^2(2b_{3g})^1$	9				
$1\,^1B_{1g}$	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^2(1a_u)^1(3b_{1u})^1$	30	−383.12079	7 (60%)	18 (13%)	3 (2%)
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^1(2b_{1u})^2(1a_u)^2(2b_{2g})^1$	26				
$3\,^1A_g$	$(1b_{1u})^2(1b_{2g})^1(1b_{3g})^2(2b_{1u})^2(1a_u)^2(2b_{2g})^1$	24	−383.10485	6 (43%)	20 (28%)	8 (4%)
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^2(1a_u)^1(2a_u)^1$	13				
$2\,^1B_{1g}$	$(1b_{1u})^2(1b_{2g})^1(1b_{3g})^2(2b_{1u})^2(1a_u)^2(2b_{3g})^1$	22	−383.08787	4 (43%)	21 (39%)	5 (2%)
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^1(1a_u)^1(2b_{3g})^2$	13				
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^1(1a_u)^2(2a_u)^1$	12				
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(1a_u)^2(2b_{2g})^1(2b_{3g})^1$	11				
$2\,^1B_{2u}$	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^1(1a_u)^2(2b_{3g})^1$	62	−383.07788	3 (81%)	11 (7%)	5 (3%)
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^2(1a_u)^1(2b_{2g})^1$	14				
$2\,^1B_{3u}$	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^2(1a_u)^1(2b_{3g})^1$	41	−383.07363	2 (83%)	8 (5%)	5(3%)
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^1(1a_u)^2(2b_{2g})^1$	42				
$1\,^3B_{2u}$	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^2(1a_u)^1(1b_{2g})^1$	59	−383.24893	5 (83%)	2 (1%)	9 (5%)
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^1(1a_u)^2(2b_{3g})^1$	13				
$1\,^3B_{3u}$	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^1(1a_u)^2(2b_{2g})^1$	40	−383.20668	3 (75%)	16 (12%)	1 (0.3%)
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^2(1a_u)^1(2b_{3g})^1$	33				
$1\,^3B_{1g}$	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^2(1a_u)^1(3b_{1u})^1$	39	−383.20394	6 (82%)	3 (1%)	6 (3%)
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^1(2b_{1u})^2(1a_u)^2(2b_{2g})^1$	37				
$2\,^3B_{2u}$	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^1(1a_u)^2(2b_{3g})^1$	57	−383.19936	3 (76%)	15 (10%)	6 (2%)
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^2(1a_u)^1(2b_{2g})^1$	19				
$1\,^3A_g$	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^1(1a_u)^2(3b_{1u})^1$	27	−383.16435	4 (80%)	9 (4%)	5 (2%)
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^1(2b_{1u})^2(1a_u)^2(2b_{3g})^1$	22				
	$(1b_{1u})^2(1b_{2g})^1(1b_{3g})^2(2b_{1u})^2(1a_u)^2(2b_{2g})^1$	19				
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^2(1a_u)^1(2a_u)^1$	12				
$2\,^3A_g$	$(1b_{1u})^2(1b_{2g})^1(1b_{3g})^2(2b_{1u})^2(1a_u)^2(2b_{2g})^1$	18	−383.12651	6 (55%)	13 (25%)	7 (2%)
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^1(1a_u)^2(3b_{1u})^1$	15				
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^2(1a_u)^1(2a_u)^1$	10				
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^1(1a_u)^1(2b_{2g})^1(2b_{3g})^1$	10				
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^1(2b_{1u})^2(1a_u)^2(2b_{3g})^1$	9				
$2\,^3B_{1g}$	$(1b_{1u})^2(1b_{2g})^1(1b_{3g})^2(2b_{1u})^2(1a_u)^2(2b_{3g})^1$	32	−383.11988	4 (57%)	14 (13%)	10 (5%)
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^1(1a_u)^2(2a_u)^1$	20				
$3\,^3A_g$	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^1(1a_u)^2(3b_{1u})^1$	35	−383.07714	4 (84%)	5 (5%)	3 (1%)
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^1(2b_{1u})^2(1a_u)^2(2b_{3g})^1$	47				
$3\,^3B_{1g}$	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^1(2b_{1u})^2(1a_u)^2(2b_{2g})^1$	46	−383.07288	4 (84%)	11 (10%)	3 (1%)
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^2(1a_u)^1(3b_{1u})^1$	31				
$4\,^3B_{1g}$	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^2(2b_{2g})^1(2b_{3g})^1$	23	−383.05098	4 (8%)	20 (69%)	7 (4%)
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^1(1a_u)^1(2b_{2g})^2$	20				
$5\,^3B_{1g}$	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^1(1a_u)^1(2b_{2g})^2$	10	−383.00159	4 (7%)	34 (69%)	3 (1.3%)
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(1a_u)^2(2b_{2g})^1(2b_{3g})^1$	7				
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^1(2b_{1u})^2(1a_u)^1(2b_{3g})^1(3b_{1u})^1$	6				
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^1(2b_{1u})^1(1a_u)^2(2b_{2g})^1(3b_{1u})^1$	3				
	$(1b_{1u})^2(1b_{2g})^1(1b_{3g})^2(2b_{1u})^2(1a_u)^1(2b_{2g})^1(3b_{1u})^1$	3				
$4\,^3A_g$	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^1(1a_u)^2(3b_{1u})^1$	17	−383.00152	6 (30%)	31 (37%)	10 (6%)
	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^1(2b_{1u})^2(1a_u)^2(2b_{3g})^1$	7				
	$(1b_{1u})^1(1b_{2g})^2(1b_{3g})^2(2b_{1u})^2(1a_u)^2(3b_{1u})^1$	7				

Table 6. Occupation numbers and $\langle z^2 \rangle$ values of the active space of naphthalene ground and excited states

State	Occupation numbers				$\langle z^2 \rangle$ (au)			
	b_{1u}	b_{2g}	b_{3g}	a_u	b_{1u}	b_{2g}	b_{3g}	a_u
$1\,^1A_g$	1.9640	1.9457	1.9234	1.8839	2.47	2.49	2.49	2.43
	1.8899	0.1211	0.1038	0.0524	2.38	1.76	1.74	1.47
	0.0753		0.0312		1.64		1.29	
$1\,^1B_{3u}$	1.9306	1.8828	1.8996	1.4764	2.48	2.49	2.48	2.39
	1.4261	0.5773	0.5422	0.1057	2.34	2.27	2.22	1.63
	0.1051		0.0542		1.74		1.38	
$2\,^1A_g$	1.9073	1.8606	1.5666	1.6869	2.48	2.48	2.45	2.41
	1.4396	0.3334	0.5291	0.1179	2.31	2.07	2.19	1.66
	0.4861		0.0725		2.54		1.49	
$1\,^1B_{2u}$	1.9694	1.9351	1.9250	1.1197	2.52	2.54	2.55	2.53
	1.8241	0.9124	0.1724	0.0401	2.43	2.85	2.17	1.58
	0.0626		0.0213		1.89		1.34	
$1\,^1B_{1g}$	1.9231	1.9024	1.5865	1.2902	2.49	2.50	2.49	2.38
	1.7188	0.7288	0.2330	0.0947	2.42	2.37	1.97	1.65
	0.4634		0.0592		2.64		1.47	
$3\,^1A_g$	1.9157	1.6144	1.8137	1.2983	2.49	2.46	2.49	2.34
	1.6014	0.8651	0.3632	0.2574	2.37	2.36	2.10	1.97
	0.2092		0.0615		2.05		1.46	
$2\,^1B_{1g}$	1.8978	1.6198	1.8422	1.6254	2.50	2.47	2.48	2.42
	1.2638	0.3964	0.8682	0.2602	2.29	2.14	2.34	1.97
	0.1551		0.0711		2.01		1.48	
$2\,^1B_{2u}$	1.9589	1.9346	1.8775	1.7269	2.52	2.54	2.52	2.47
	1.2119	0.2824	0.7936	0.0598	2.43	2.25	3.14	1.61
	0.1283		0.0261		2.19		1.58	
$2\,^1B_{3u}$	1.9578	1.9536	1.9161	1.4389	2.52	2.56	2.57	2.43
	1.4625	0.5815	0.5333	0.0482	2.39	2.59	3.37	1.64
	0.0781		0.0300		1.77		1.38	
$1\,^3B_{2u}$	1.9490	1.9079	1.8339	1.2558	2.48	2.49	2.48	2.32
	1.7479	0.7476	0.2528	0.0914	2.37	2.28	1.95	1.59
	0.1671		0.0467		1.90		1.36	
$1\,^3B_{3u}$	1.9426	1.8858	1.8875	1.5049	2.49	2.50	2.49	2.40
	1.4356	0.5774	0.5012	0.1052	2.34	2.28	2.26	1.68
	0.1143		0.0456		1.79		1.38	
$1\,^3B_{1g}$	1.9349	1.9046	1.4972	1.4697	2.46	2.49	2.44	2.38
	1.8792	0.5285	0.1301	0.0903	2.37	2.19	1.77	1.60
	0.5116		0.0538		2.42		1.45	
$1\,^3A_g$	1.9334	1.7212	1.6730	1.7416	2.49	2.46	2.47	2.43
	1.5909	0.3336	0.3596	0.2040	2.34	2.07	2.13	1.88
	0.3889		0.0539		2.44		1.45	
$2\,^3A_g$	1.8935	1.7117	1.7990	1.5191	2.49	2.47	2.48	2.39
	1.4511	0.5737	0.4955	0.1984	2.34	2.23	2.13	1.85
	0.2816		0.0764		2.23		1.50	
$2\,^3B_{1g}$	1.9309	1.5372	1.8405	1.6211	2.49	2.43	2.48	2.40
	1.4507	0.4044	0.6743	0.3318	2.34	2.12	2.27	2.01
	0.1533		0.0559		1.90		1.42	
$3\,^3A_g$	1.9681	1.9372	1.4394	1.8542	2.53	2.53	2.52	2.48
	1.5395	0.1530	0.6005	0.6008	2.42	2.01	2.70	1.66
	0.4249		0.0225		3.80		1.45	
$3\,^3B_{1g}$	1.9616	1.9357	1.4488	1.5376	2.51	2.51	2.55	2.51

Table 6—continued

State	Occupation numbers				$\langle z^2\rangle$ (au)			
	b_{1u}	b_{2g}	b_{3g}	a_u	b_{1u}	b_{2g}	b_{3g}	a_u
	1.8347	0.6662	0.1200	0.0710	2.41	2.54	1.90	1.67
	0.3987		0.0258		21.08		1.43	
$4\,^3\mathrm{B}_{1g}$	1.9046	1.7993	1.6515	1.0165	2.49	2.49	2.45	2.31
	1.4589	1.0226	0.6303	0.1635	2.34	2.42	2.29	1.79
	0.2819		0.0712		2.14		1.50	
$5\,^3\mathrm{B}_{1g}$	1.8460	1.6360	1.5115	1.4078	2.47	2.45	2.43	2.37
	1.3971	0.5945	0.7303	0.2817	2.31	2.23	2.34	1.94
	0.4914		0.1037		2.40		1.63	
$4\,^3\mathrm{A}_g$	1.6106	1.7191	1.6225	1.5584	2.39	2.47	2.46	2.40
	1.5568	0.5341	0.4015	0.1837	2.41	3.60	2.07	1.82
	0.6347		0.1787		2.69		2.01	

for the v_{0-0} energy [43], while a two-photon excitation spectrum (TPES) [17, 44] gives the energy 4.12 eV for the most intense peak in this band. The transition is very weak with a computed oscillator strength of only 0.001. The corresponding experimental value is 0.002 [43, 45]. The wave function for this state can be described as an almost equal mixing of two singly excited configurations ($1a_u \rightarrow 2b_{3g}$) and ($2b_{1u} \rightarrow 2b_{2g}$), with only a moderate fraction of doubly excited states mixed in (cf. Table 5).

Table 7. Naphthalene ground and excited states quadrupole moments in atomic units

State	Q_{zz}	Q_{xx}	Q_{yy}
$1\,^1A_g$	−8.35	−2.98	11.34
$1\,^1B_{3u}$	−7.62	−3.48	11.10
$2\,^1A_g$	−7.40	−3.14	10.54
$1\,^1B_{2u}$	−8.76	−3.95	12.71
$1\,^1B_{1g}$	−7.76	−3.58	11.34
$3\,^1A_g$	−7.44	−3.60	11.04
$2\,^1B_{1g}$	−7.34	−3.04	10.39
$2\,^1B_{2u}$	−8.52	−3.00	11.52
$2\,^1B_{3u}$	−7.73	−5.28	13.00
$1\,^3B_{2u}$	−7.69	−3.91	11.60
$1\,^3B_{3u}$	−7.94	−2.75	10.68
$1\,^3B_{1g}$	−7.52	−4.07	11.59
$2\,^3B_{2u}$	−7.57	−3.35	10.92
$1\,^3A_g$	−7.70	−2.45	10.15
$2\,^3A_g$	−7.18	−3.51	10.69
$2\,^3B_{1g}$	−7.44	−3.10	10.54
$3\,^3A_g$	−8.42	−3.66	12.08
$3\,^3B_{1g}$	−14.76	0.48	14.28
$4\,^3B_{1g}$	−7.13	−4.70	11.83
$5\,^3B_{1g}$	−6.75	−4.00	10.75
$4\,^3A_g$	−7.08	−2.77	9.85

Table 8. Naphthalene CASSCF (S–S) and (T–T) excitation energies, transition moments and (oscillator strengths) compared with experimental results

State	CASSCF		Experiment
	ΔE (eV)	Trans. moment (f)	ΔE (eV) (f)
$1\,^1A_g$	0.0		
$1\,^1B_{3u}(x)$	4.5	0.0967 (0.001)	4.0 (0.001)^a; 3.97 (0.002)^b; 4.12^{c,d}
$2\,^1A_g$	6.0		5.5^c
$1\,^1B_{2u}(y)$	6.7	0.7834 (0.10)	4.8 (0.11)^a
$1\,^1B_{1g}$	6.9		5.2^c
$3\,^1A_g$	7.3		6.1^c
$2\,^1B_{1g}$	7.8		
$2\,^1B_{2u}(y)$	8.0	1.5925 (0.50)	7.5^a; 7.4 (0.8)^{e,f}
$2\,^1B_{3u}(x)$	8.2	3.1188 (1.94)	6.0 (1.3)^b
$1\,^3B_{2u}$	0.0		
$2\,^3B_{3u}$	1.1		1.2^j
$1\,^3B_{1g}(x)$	1.2	0.0420 (10^{-4})	1.30–1.35 ($<2\times10^{-4}$)^g
$1\,^3A_g\,(y)$	2.3	0.0903 (0.5×10^{-3})	2.25^h
$2\,^3A_g\,(y)$	3.3	0.1362 (0.002)	2.93^h; 2.0–2.5 (0.002)^g
$2\,^3B_{1g}(x)$	3.5	0.0311 (10^{-4})	
$3\,^3A_g\,(y)$	4.7	0.0390 (0.2×10^{-3})	
$3\,^3B_{1g}(x)$	4.8	1.0885 (0.14)	3.12^h (0.14)^i; 3.00 (0.12)^g
$4\,^3B_{1g}(x)$	5.4	0.2038 (0.005)	
$5\,^3B_{1g}(x)$	6.7	0.0233 (10^{-4})	
$4\,^3A_g(y)$	6.7	0.0889 (0.001)	

[a] Energy-loss, vapor [16]
[b] Absorption, vapor [43]
[c] Two-photon, solution [17]
[d] Two-photon, solution and crystal [44]
[e] Absorption, solution and vapor [4]
[f] Absorption, solution and vapor [11]
[g] Absorption, solution [13]
[h] Absorption, vapor [14]
[i] Absorption, vapor [6]
[j] Absorption crystal [8]

The $1\,^1B_{3u}$ state can be characterized as a "minus" state in Pariser's notation [18] even at this level of theory, since the two singly excited configurations have even at this level of theory, since the two singly excited configurations have almost the same coefficients with opposite signs. Strictly, the classification into "plus" and "minus" states is only valid within the framework of the PPP approximation. For some of the states reminiscenses of this symmetry can, however, also be seen here, as a glance at Table 5 shows. The $1\,^1B_{3u}^-$ state is mainly covalent, which explains the good agreement obtained for the excitation energy: the calculations on benzene showed a strong correlation between the ionic character of the state and the importance of σ-π correlation effects.

The second excited singlet state is of A_g symmetry with a computed excitation energy of 6.0 eV. Excitation to this state is dipole forbidden and it has not been observed in single photon experiments. We note that the computed energy is probably too high, but since this state can also be approximately labelled as "minus" we expect the error in the excitation energy to be less than 1.0 eV. Dick and Hohlneicher found in their TPES a peak at 5.5 eV which they assign as ^1A_g

based on the value for the two-photon polarization parameter [17]. A shoulder found at 5.2 eV is assigned to the $^1B_{1g}$ state. We compute the energy of this state to be 6.9 eV, thus indicating the reverse ordering, as has been suggested by other authors [45].

The third excited singlet state has B_{2u} symmetry. It is thus dipole allowed (y polarization) with a computed oscillator strength of 0.10. The only possible assignment is to the peak at 4.8 eV in the energy-loss spectrum [16], for which an oscillator strength of 0.11 has been measured. Thus, the error in the computed excitation energy amounts to 1.9 eV. We attribute around 0.5 eV of the error to the lack of radial correlation (π-π) and around 1.0 eV to σ-π correlation effects. Nakatsuji et al. [30] have also studied this state. Their computed excitation energy is 6.0 eV when only π-electrons are correlated. Including σ-orbitals into the CI space reduces the energy to 5.4 eV. These results confirm the error estimates made in the present work. The wave function is dominated by the singly excited configuration ($1a_u \rightarrow 2b_{2g}$) and cannot be classified as a plus or minus state.

Three states of g symmetry are found in the energy range between 7.0 and 8.0 eV. Transitions to these states are dipole forbidden. It is not impossible that some of the weak features observed in the spectrum between 6.0 and 7.0 eV [16] could be attributed to one or more of these transitions. A conclusive assignment is, however, not possible, due to both the uncertainty in the calculated transition energies and the complexity of the spectrum in this energy region. However, a ^1A_g state has been found at 6.1 eV in the TPES by Dick and Hohlneicher [17]. The shoulder found in the same spectrum at 5.2 eV could be attributed to the $2\,^1B_{1g}$ state which is computed to lie 6.9 eV above the ground state. The wave functions for two of the states show considerable contributions from doubly excited CSF's: 39% in $2\,^1B_{1g}$ and 28% in $3\,^1A_g$ (cf. Table 5). A calculation which does not include these states even at the lowest level of theory is bound to fail. In a CI calculation with the aim of including σ-π correlation effects it is necessary to include the most important of these doubly excited CSF's into the reference space. A similar type of interaction was found for the $^1E_{2g}$ state in benzene (cf. Table III in [31]).

Two states are found in the region around 8.0 eV: the $2\,^1B_{2u}$ state with an oscillator strength, f, of 0.50 and the $2\,^1B_{3u}$ state with $f = 1.94$. The latter state clearly corresponds to the sharp peak found in the spectrum around 6.0 eV, which has a measured oscillator strength of 1.3 [43]. The assignment of the $2\,^1B_{2u}$ state is less straightforward. George and Morris [43] suggest that the shoulder around 6.1 eV on the high energy side of the intense peak could be attributed to a $^1B_{2u}$ excitation. They do not, however, rule out other possibilities. Huebner et al. find in their energy-loss spectrum [16] a broad band with a peak around 7.5 eV. This region contains a number of Rydberg transitions but the broadness and intensity of the band does indicate an overlapping valence excitation in this region. Earlier absorption spectra of naphthalene in solution also show a feature around 7.4 eV which has tentatively been assigned to B_{2u} [4, 11]. A rather uncertain oscillator strength of 0.8 has been reported [4]. This value fits nicely with the computed value of 0.5, which we believe to be reasonably accurate.

In conclusion we have found four allowed transitions in the energy interval up to 8.0 eV, and in addition four symmetry forbidden transitions. Our assignment of the allowed transitions is in agreement with the assignments made by Mann et al. [4] for the solution spectra, and also explains the dominant features in the energy-loss spectrum of Huebner et al. [16]. With these assignments the error in computed vertical excitation energies range from 0.5 to 2.0 eV, while computed oscillator strengths are in agreement with experimentally deduced values. These results are consistent with the experience gained in the previous study of the benzene molecule.

3.2. The triplet states

The lowest triplet state of naphthalene was first investigated by Lewis and Kasha [1] and McClure [2], who assigned it to B_{2u} symmetry. All previous semiempirical calculations have also found the lowest triplet to be a B_{2u} state, and it has been convincingly established in a paramagnetic resonance absorption experiment [7].

In agreement with these earlier results, the lowest triplet state found in the present study has B_{2u} symmetry. The computed vertical excitation energy from the singlet ground state is 3.4 eV to be compared with the experimental value of 2.64 eV [2]. The two earlier *ab initio* results reported for this state yielded excitation energies of 4.7 eV [28] and 4.3 eV [29], respectively. The former result was obtained from an SCF calculation performed by Hinchliffe and the latter is a CI result obtained by Ha and Wild. Despite the lowering of the excitation energy by 0.9-1.3 eV compared to the earlier results, the CASSCF energy difference is still almost 0.8 eV above the experimental value. The lowest triplet energies in benzene were already in good agreement with experiment at the CASSCF level of theory [31]. The larger error obtained here is therefore most likely due to basis set deficiencies.

The $1\,^3B_{2u}$ state is described mainly by the single excitations ($1a_u \rightarrow 2b_{2g}$) and ($2b_{1u} \rightarrow 2b_{3g}$). They contribute to the wave function with weights of 59% and 13%, respectively (cf. Table 5). This state is used as the reference point for the T-T excitations in naphthalene. In all, CASSCF calculations have been performed for twelve triplet states in the energy range 0.0-7.0 eV. The electric dipole allowed transitions (from the $1\,^3B_{2u}$ state) are those having B_{1g} and A_g symmetry.

Hanson and Robinson [8] have detected a weak band in the crystalline naphthalene $T \leftarrow S_0$ spectrum located 1.2 eV above the lowest triplet. Based on Pariser's PPP results [18] it was assumed to correspond to the third triplet state with symmetry $^3B_{3u}^+$. Later Meyer et al. [13] performed PPP calculations including doubly excited configurations and obtained a different order of the lower triplets, where the $^3B_{3u}^+$ state was the second triplet state.

The present CASSCF results show a more complex picture with three states in the energy range 1.1-1.3 eV (cf. Table 8) above the lowest triplet state. The $2\,^3B_{2u}$ state at 1.3 eV could borrow intensity from the lowest singlet excited state of B_{3u} symmetry. The intensity of this state is, however, very low ($f = 0.001$). The $1\,^3B_{3u}$ state at 1.1 eV borrows its intensity from the stronger $^1B_{2u}$ absorption at 4.7 ($f = 0.10$), while the $^3B_{1g}$ state at 1.2 eV cannot obtain any intensity from the allowed

$S_n \leftarrow S_0$ transitions. The most likely assignment of the weak band found by Hanson and Robinson is then $^3B_{3u}$ which agrees with their own conclusions. It is interesting to note that the semiempirical calculations by Meyer et al. [13] only gave two triplet states in the energy range 1.0-1.5 eV.

The 1 $^3B_{1g}$ state represents a weakly allowed transition in the T-T spectrum, with a calculated oscillator strength of 10^{-4}. This band has not been found experimentally. Based on their spectra for anthracene and naphthalene and semiempirical calculations Meyer et al. [13] have estimated the first $^3B_{1g}$ state to be located at 1.30-1.35 eV in the T-T spectrum with a oscillator strength $f < 2 \times 10^{-4}$, in essential agreement with the present results. The transition is forbidden in PPP theory (a plus state) while the CASSCF results predict it to be weakly allowed, even though the two dominant configurations at this level of theory have almost equal weight (cf. Table 5). This state is well described by single excitations. The weight of higher excitations is only 4%. For 1 $^3B_{3u}$ and 2 $^3B_{2u}$ much higher contributions from double excitations are found: 12 and 10%, respectively, which explains the different order of these triplet states obtained in the semiempirical work of Meyer et al. [13] compared to the original PPP treatment of Pariser [18]. We notice also that these low lying triplet states are not found in the earlier *ab initio* study of Ha and Wild [29], who reported the lowest T-T transition at 2.27 eV.

The triplet-triplet absorption spectrum of naphthalene in the region between 3500 and 6000 Å (3.5-2.1 eV) has been studied extensively [13]. It is divided into two parts. In the lower energy range (2.1-2.8 eV) it consists of a weak band with four lines, and in the higher energy range there is a strong band with three lines [12, 13]. The first weak band has been assigned by Melhuish [10a] and Novak and Windsor [10b] as the $^3A_g^+ \leftarrow {}^3B_{2u}^+$ "forbidden" transition. However, Pavloupolos [12] has showed that this band has a mixed polarization indicating the existence of a state of $^3B_{1g}$ symmetry in this region. He also found that some lines correspond to the $^3A_g^- \leftarrow {}^3B_{2u}^+$ allowed transition with the 0, 0 band located at 2.5 eV [12]. Melhuish estimated an oscillator strength of 0.002 for this transition. Gas-phase experiments show two transitions at 2.25 and 2.93 eV [14], which have been assigned as $^3A_g^+$ and $^3A_g^-$.

The CASSCF calculations locate three triplet states in the energy region 2.3-3.5 eV corresponding to T-T energies of 2.3, 3.3 (^3A_g), and 3.5 eV ($^3B_{1g}$). Based on the computed energies and oscillator strengths they are assigned to the transitions found in the 4300-6000 Å region of the experimental spectrum [12, 13]. The first ^3A_g state at 2.3 eV has an oscillator strength of 0.5×10^{-3}, in good agreement with the gas phase result [14]. This CASSCF triplet state is described by four singly excited configurations that contribute 80% of the wave function.

The strongest transition in this region is located at 2.93 eV in the gas-phase spectrum [14]. A series of bands ranging from 2.0 to 2.5 eV found in solution [12] can be assumed to correspond to the same transition with a measured oscillator strength of 0.002 [13]. The present calculation gives a ^3A_g state at 3.3 eV which is described by a mixture of singly (55%) and doubly (25%) excited configurations. The computed oscillator strength is 0.002.

The $^3B_{1g}$ state found at 3.5 eV with a computed oscillator strength of 0.1×10^{-3}, can explain the polarization results of Pavloupolos [12] for this region of the spectrum. He found mixed polarization directions, which was attributed to vibronic coupling between the ^3A_g states and higher $^3B_{1g}$ states. Even if this possibility cannot be ruled out, it is not needed to explain the results, since the present calculations predict the existence of a $^3B_{1g}$ state in this region. The corresponding wave function is described as a mixture of singly (57%) and doubly (23%) excited configurations with a significant contribution (5%) from triply excited configurations.

In the higher energy part of the spectrum there is a strong absorption band that has been located at 3.12 eV in the gas-phase experiment [14] with a measured oscillator strength of 0.14. The polarization spectrum of Pavloupolos [12] shows that the transition is $^3B_{1g}^-\leftarrow{}^3B_{2u}^+$. The 0, 0 band was located at 3.00 eV. The corresponding band in alcohol solution was found at the same energy, with an oscillator strength of 0.12 [13].

The CASSCF calculations locate this state as $^3B_{1g}$ with an energy of 4.8 eV above the lowest triplet state. The calculated oscillator strength is 0.14, in good agreement with experiment. The assignment of this state to the band at 3.12 eV is therefore quite clear, even though the error in the computed transition energy (1.7 eV) is large. The corresponding wave function is described by two singly excited configurations with a summed weight of 77%, while the most important doubly excited configurations contribute with 10%. The occupation numbers and orbital averages $\langle z^2\rangle$ given in Table 6 shows that one of the orbitals in this state is very diffuse with $\langle z^2\rangle=21.1$. This very large value indicates a mixing of valence and Rydberg configurations. An analysis of the molecular orbital $3b_{1u}$ clearly shows it to be a $3p$ type orbital. It is more diffuse than any of the valence orbitals found for the diffuse states in benzene [31].

Meyer et al. [13] did not discard the possibility of more transitions occurring in the energy range 3.0–4.0 eV. The calculations indicate the existence of a ^3A_g with a computed T-T transition energy of 4.7 eV and an oscillator strength of 0.2×10^{-3}. It is not possible to give a precise estimate of the error in the computed energy. Therefore we cannot predict the exact location of this state. Due to its weakness it is in any case not likely to be found in experiment, since it occurs in a region with strong absorption from other triplet states.

4. Discussion

An attempt has been made in the present work to use the CASSCF method to interpret the electronic spectrum of naphthalene. It was clear from the outset, that a method which only takes into account electron correlation within the valence π-orbitals will yield too large excitation energies. Errors between 0.0–2.0 eV were expected. The errors have three different origins: (1) basis set deficiencies, (2) incomplete π-electron (radial) correlation and (3) neglect of σ-π correlation effects. The results obtained for benzene indicate that all these effects will lower the energies of the excited states. There is thus no cancellation of errors, which explains the rather large deviations from experiment found for some states.

A strong correlation between the ionic character of the excited states and the effect of σ-π correlation effects was found in the earlier study of the benzene molecule [31]. The ionic character could be identified by the diffuseness of the orbitals. Thus $\langle z^2 \rangle$ for the $1e_{2u}$ orbital was 2.64 in the $^1B_{2u}$ state, 6.37 in $^1B_{1u}$ and as large as 15.87 in $^1E_{1u}$ (cf. Table IV in [31]). Such large variations in the radial extension of the orbitals have not been found in naphthalene (cf. Table 6). The largest value found for a valence orbital is 3.80 (the orbital $3b_{1u}$ in $3\,^3A_g$). It is likely that the larger size of the molecule diminishes the electron repulsion terms which cause the orbitals to become diffuse. Part of the difference may, however, be due to the different type of basis set used in the present work, which is slightly less diffuse than the basis used for benzene.

Due to the rather large errors obtained for some of the excitation energies, assignments have been based on a combination of energies and transition moments. The present study has confirmed our earlier conclusion [31] that transition moments are rather accurately predicted at the CASSCF level of theory, and consequently less affected by the dynamic correlation effects, which are so important for accurate predictions of relative energies. Thus it has been possible to assign all of the dipole allowed transitions in the energy region up to 6.0 eV. Dipole forbidden transitions cause more problems, and it was not possible to discriminate completely between the g-g transition found in the TPES by Dick and Holneicher [17] in the energy region 5.0-6.0 eV.

It might be argued from the results obtained in the present study, that CASSCF is not the appropriate method for calculations of excitation energies for larger aromatic systems, like naphthalene. Actually, better agreement with experiment is obtained with simpler methods like CNDO-CI [17]. However, such a simple comparison is misleading. The errors appearing in semiempirical calculations are statistical and based on some parameter fitting and therefore unverifiable. *Ab initio* work on the other hand give errors which are systematic and have identifiable sources. A calculation can therefore be used to set the error bars appropriate for the level of theory used and to point to the future direction which should be taken in order to improve the results. It is, for example, clear that the major part of the error in computed transition energies obtained in the present study is due to the neglect of dynamic electron correlation effects, the most important part being due to σ-π interactions. This points to possible ways of improving the calculations of these properties, but it also tells us that properties that are less affected by dynamic electron correlation should be essentially correct at the present level of theory. The transition moments, and the quadrupole moments belong to this category. In addition the major features of the electronic structure of the different excited states are well reproduced by the CASSCF wave functions (Tables 5 and 6).

The results obtained in the present work can be improved by including the missing correlation effects. The most straightforward way to do that is by means of multi-reference (MR) CI calculations. The size of the basis set would have to be further extended in order to account properly for the slowly convergent intra-atomic correlation effects, and cluster corrections must be included (e.g. by the coupled-pair functional method). The size of such calculations are beyond the computational capacity presently available at this laboratory, but considering the continuous development of MR-CI methods we expect such calculations to be quite feasible in the near future.

Acknowledgements. The research reported in this communication has been supported by a grant from the Swedish Natural Science Research Council (NFR) and by IBM Sweden under a joint study contract. J.M.O.M. acknowledges support from the Brazilian Agency CAPES.

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