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An *ab initio* Study of the Ground and Excited States of *p*-Benzoquinone

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The results of an *ab initio* SCF calculation for the ground state and CI calculations for the excited states of *p*-benzoquinone are presented and discussed. A minimum basis set of Slater type orbitals was employed and the CI calculations were performed by considering single excitations from valence to virtual SCF molecular orbitals. The convergence of the calculated excitation energies is studied as a function of the number of orbitals used in the CI calculations. These calculations explain quite well the experimental results.

Key words: p-benzoquinone – Excited states of *p*-benzoquinone

1. Introduction

Quinones are an important class of compounds for biological systems [1]. The parent of these compounds is *p*-benzoquinone (PBQ) and its electronic structure and spectra are, therefore, of much interest.

Experimentally, the photoelectron spectrum of PBQ has been measured by two groups of workers [2, 3], and recent spectroscopic studies of PBQ [4–8] have determined the low-lying singlet and triplet $n \rightarrow \pi^*$ excited states and the $\pi \rightarrow \pi^*$ excited singlet states which lie at slightly higher energies. Of particular interest is the magnitude of the splittings between the two $n \rightarrow \pi^*$ singlet → singlet and singlet → triplet transitions and the positions of the $\pi \rightarrow \pi^*$ triplet states relative to the two $n \rightarrow \pi^*$ triplet states.

Many simple theoretical treatments of this molecule have been considered [9–13] and, more recently, the CNDO method has been used [14–16]. During the later stages of the present work, which is intended to give an *ab initio* description of the ground and excited states of PBQ, the results of another *ab-initio* study of these states became available [17]. In this latter study a small, (6, 3/3), basis of gaussian functions was contracted to [4, 2/2] and ground and excited states were obtained by the restricted self-consistent field (SCF) method using both a delocalised description, where the full D_{2h} symmetry was imposed for the SCF calculations (ΔSCF(D_{2h})), and a localised description, where only C_{2v} symmetry was imposed for the SCF calculations (ΔSCF(C_{2v})). It is of interest to compare our results, presented below, with the results of this study since a different methodology has been applied in the two cases. We also compare the calculated results with those obtained from experiment.

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2. Method and Computational Details

The excited states of PBQ have been calculated using the singly excited configuration interaction (CI) method [18, 19]. Pople and co-workers [20, 21] have employed this CI approach for calculating the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excited states of small molecules and have suggested considering all excitations from the M highest occupied to the M lowest virtual molecular orbitals (MO) with M to be determined. For our study of the excited states of PBQ we calculated excitation energies for $M = 4$ to 16 (equals the total number of virtual orbitals with our basis set). The largest CI matrix we encounter has thus the dimensions of 256×256.

The basis set employed for the calculations was that due to Pople and co-workers [22] and consisted of a minimal basis of Slater type orbitals (STO) with standard orbital exponents, each STO being represented by a sum of four gaussian functions, chosen according to the least squares criterium. Such a basis is expected to give adequate results for $n \rightarrow \pi^*$ transitions and for triplet $\pi \rightarrow \pi^*$ transitions but poorer results for singlet $\pi \rightarrow \pi^*$ transitions [20], due in part to the sensitivity of the exchange integral $K_{\pi\pi^*}$ to the basis set.

The geometry used for the calculations was as determined by Trotter [23]. The molecule has D_{2h} symmetry and we have chosen it to lie in the xy plane with the y axis coinciding with the carbonyl groups.

3. Results and Discussion

The description obtained from the ground state calculation for the four highest occupied and four lowest virtual MO's is similar to that obtained from previous CNDO calculations [14] (see Table IA of Ref. [4]), although the orbital orderings are slightly different. Of the two n MO's the orbital of b_{1g} symmetry is at higher energy and is found to be more delocalized than the second n MO of b_{3u} symmetry. We have calculated this orbital separation as 0.72 eV. In Table 1 we

Table 1. Calculated and experimental ionization energies for PBQ (in eV)

Orbital		Orbital energies[a]		ΔSCF[b]		Experiment[c]
Number	Symmetry designation	A	B	D_{2h}	C_{2v}	
28	$2b_{1u}$	8.30	10.91	10.42	10.06	10.11
27	$4b_{1g}$	9.23	11.75	11.04	8.60	10.41
26	$1b_{2g}$	9.67	11.37	10.53	10.06	11.06
25	$5b_{3u}$	9.95	12.35	11.23	8.60	11.25
24	$1b_{3g}$	12.66	14.91	14.20	14.20	13.43
23	$8a_g$	13.55	16.02	15.45	13.40	14.4
22	$3b_{1g}$	14.11				15.0
21	$1b_{1u}$	14.43				15.6
20	$7b_{2u}$	14.46	16.84	16.08	13.40	16.4

[a] A refers to the results of this study and B to the results given in Ref. [17].

[b] Reference [17], D_{2h} and C_{2v} refer to the symmetry imposed for the SCF calculations.

[c] References [2, 3], assignments not definite.

Table 2. Calculated excitation energies (in eV) as a function of M^a for the low-lying excited states of PBQ

Excited state and transition type	$M=4$	7	12	13	16
Singlets					
$^1B_{2g}\,(n\rightarrow\pi^*)$	3.95	3.53	3.51	3.38	3.36
$^1A_u\,(n\rightarrow\pi^*)$	4.15	3.76	3.75	3.57	3.55
$^1B_{1g}\,(\pi\rightarrow\pi^*)$	7.92	7.87	7.79	7.69	7.50
$^1B_{2u}\,(\pi\rightarrow\pi^*)$	8.62	8.55	8.14	8.14	7.94
$^1B_{3g}\,(\sigma\rightarrow\pi^*)$		9.88	8.23	8.16	8.13
Triplets					
$^3B_{2u}\,(\pi\rightarrow\pi^*)$	3.12	2.50	1.86	1.86	1.84
$^3B_{2g}\,(n\rightarrow\pi^*)$	3.11	2.56	2.55	2.38	2.35
$^3A_u\,(n\rightarrow\pi^*)$	3.26	2.80	2.79	2.55	2.52
$^3B_{1g}\,(\pi\rightarrow\pi^*)$	4.27	4.30	3.50	3.50	3.46
$^3A_g\,(\pi\rightarrow\pi^*)$		5.29	3.95	3.95	3.93
$^3B_{2u}\,(\pi\rightarrow\pi^*)$	7.75	7.14	5.03	5.03	5.01
$^3B_{3g}\,(\sigma\rightarrow\pi^*)$		9.41	6.94	6.89	6.80
$^3B_{1u}\,(\sigma\rightarrow\pi^*)$			7.10	7.10	7.00

[a] Excitations are considered from the M highest occupied to the M lowest virtual MO's.

list the orbital energies calculated for the first nine orbitals and compare the results with the results of previous *ab-initio* calculations [17] and with the experimental photoelectron spectrum, the assignment of which is not conclusive. The ordering of the four highest occupied MO's is yet again different from these latter calculations, with a calculated orbital splitting for the n MO's of 0.60 eV. This splitting is reduced to 0.19 eV when ΔSCF calculations are performed imposing D_{2h} symmetry and becomes zero when the symmetry is relaxed to C_{2v}. From theoretical results so far obtained the assignment of the photoelectron spectrum must be considered tentative and a more reliable assignment must therefore wait for more accurate theoretical results.

In Table 2 we show the calculated excitation energies for several values of M. It is obviously desirable, if possible, to find some criterium for truncating the CI expansion for molecules of the size of PBQ. However, such a procedure cannot be generally adopted since although results sometimes appear to have converged the addition of more orbitals to the CI will again lower the calculated excitation energies. An example of this is given for the two $n\rightarrow\pi^*$ singlets, $^1B_{2g}$ and ^1A_u. For $m=7$ to 12 the excitation energies remain essentially constant but in going from $M=12$ to 13 the excitation energies drop by 0.13 and 0.18 eV respectively.

The results of our calculations for the excitation energies are compared with the results of previous calculations [17] and with experimental results [4–8] in Table 3. The calculated components of the CI wave functions are also given in this table. The first point to note is that our calculations and the ΔSCF (D_{2h}) calculations produce the correct ordering for all the six experimentally observed states (the ΔSCF (C_{2v}) calculations obviously do not reproduce the important splittings), our excitation energies being in better agreement with experiment for

Table 3. Calculated and experimental excitation energies (in eV) and calculated excited state wave functions for the low-lying excited states of PBQ

Excited states and transition types	Excitation energies					Components of CI wave functions (in %)[c]
	without CI	with CI	ΔSCF[a] D_{2h}	ΔSCF[a] C_{2v}	Experiment[b]	
Singlets						
$^1B_{2g}(n\rightarrow\pi^*)$	5.57	3.36	4.59	2.08	2.48	22(25→31); 69(27→29)
$^1A_u(n\rightarrow\pi^*)$	6.08	3.55	4.67	2.08	2.52	69(25→29); 22(27→31)
$^1B_{1g}(\pi\rightarrow\pi^*)$	7.95	7.50	5.42	5.24	4.07	94(26→29)
$^1B_{2u}(\pi\rightarrow\pi^*)$	8.74	7.94	7.13	5.24	5.13	94(28→29)
$^1B_{3g}(\sigma\rightarrow\pi^*)$	10.05	8.13				14(20→31); 72(23→29)
Triplets						
$^3B_{2u}(\pi\rightarrow\pi^*)$	4.09	1.84	2.49	2.49		11(24→31); 10(26→30); 74(28→29)
$^3B_{2g}(n\rightarrow\pi^*)$	5.07	2.35	4.21	1.85	2.28	6(22→29); 24(25→31); 66(27→29)
$^3A_u(n\rightarrow\pi^*)$	5.56	2.52	4.34	1.85	2.32	5(22→31); 66(25→29); 23(27→31)
$^3B_{1g}(\pi\rightarrow\pi^*)$	6.19	3.46	4.25	4.25		7(21→30); 55(26→29); 8(26→32); 29(28→30)
$^3A_g(\pi\rightarrow\pi^*)$	8.08	3.93				12(21→31); 52(24→29); 6(24→32); 31(28→31)
$^3B_{2u}(\pi\rightarrow\pi^*)$	7.73	5.01	6.75	6.75		29(21→29); 12(24→31); 44(26→30); 14(28→32)
$^3B_{3g}(\sigma\rightarrow\pi^*)$	9.63	6.80				8(17→29); 20(20→31); 61(23→29)
$^3B_{1u}(\sigma\rightarrow\pi^*)$	10.30	7.00				7(17→31); 7(18→29); 58(20→29); 20(23→31)

[a] Reference [17], D_{2h} and C_{2v} refer to symmetry imposed for SCF calculations.

[b] References [4, 5].

[c] Only given if ≥ 5 %. The corresponding orbital excitations are given in parenthesis where the orbital numbering is according to Table 1 for the occupied MO's and for the virtual MO's is $2b_{3g}$ (29), $1a_u$ (30), $3b_{1u}$ (31) and $3b_{3g}$ (32).

the $n\rightarrow\pi^*$ states. Our calculated magnitude for the splittings of the two $n\rightarrow\pi^*$ singlet→singlet and singlet→triplet transitions are 0.19 and 0.17 eV respectively, the corresponding experimental values being ~0.03 and 0.04 eV. The ΔSCF (D_{2h}) values are respectively 0.082 and 0.13 eV for these splittings. The splittings between corresponding singlet and triplet states are ~ 1.0 eV compared to an experiment value of ~0.2 eV and the ΔSCF (D_{2h}) value of ~0.4 eV. We have calculated the lowest triplet state to be the $^3B_{2u}$ ($\pi\rightarrow\pi^*$) state in agreement with the ΔSCF (D_{2h}) calculations. However, the ΔSCF (C_{2v}) calculations resulted in this state being placed above the two triplet $n\rightarrow\pi^*$ states. Experimentally the position of this $^3B_{2u}$ state is not known. As expected the greatest error in our calculated results occurs for the singlet $\pi\rightarrow\pi^*$ states [20].

4. Conclusions

Although the results presented herein do not offer a completely reliable interpretation and understanding of the experimental results for PBQ we feel that they are as reasonable as any available at present. The CI method we have employed for the calculation of the excited states gives promising results and describes the main spectral features reasonably well, and in the manner expected from previous studies [20, 21]. The main deficiency of the present calculations is the use of a small inflexible basis set. Of course, the size of the molecule does not permit the use of very large bases.

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