J. Phys. Chem. A **1997,** *101,* 4449−4459

Density-Functional Studies on the Structure and Vibrational Spectra of Transient Intermediates of *p*-Benzoquinone

Pothukattil Mohandas and Siva Umapathy*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

Received: January 9, 1997; In Final Form: March 21, 1997[⊗]

Prediction of vibrational frequencies of polyatomic molecules using density-functional theory (DFT) methods has become common because of its accuracy and therefore consistency with experimental data. However, the utility of DFT methods in predicting vibrational frequencies and normal mode descriptions of excited state intermediates has not been addressed so far. In this paper we have evaluated the performance of Hartree−Fock (HF) and various density-functional (DF) and hybrid Hartree−Fock/density-functional (HF/DF) methods in predicting the structure, vibrational frequencies, and normal mode descriptions of transient intermediates, taking *p*-benzoquinone (BQ) as an example. The structures, bond orders, harmonic vibrational frequencies, and isotopic shifts for BQ and its lowest triplet state, semiquinone radical, and semiquinone radical anion have been calculated using all of these methods employing 6−31G(d) and 6−31G(d,p) basis sets. Assignments of the calculated vibrational frequencies were made with the help of normal mode analysis. The calculated structural parameters and bond orders indicate that the structure of the triplet state is intermediate between those of the ground state and radical anion. The semiquinone radical shows a mixed aromatic and quinonoid structure. Geometrical changes involved in the triplet excited state and semiquinone radical anion with respect to ground state structure are explained on the basis of the calculated electronic structures. Of all the methods tested, the three parameter hybrid HF/DF methods (B3LYP, B3P86, and B3PW91) were found to give the most accurate geometries. These methods are also found to reproduce the experimental frequencies of the ground state as well as transient species within 2−4% error, whereas the isotopic shifts calculated for the deuterated species using the BP86 method are superior and show excellent agreement with experiment. Calculations using all of the methods show that both 6-31G(d) and 6-31G(d,p) basis sets yield very similar results.

Introduction

Prediction of vibrational frequencies for ground state molecules from density-functional (DF) and hybrid Hartree−Fock/density-functional (HF/DF) methods has become routine.[1−18] Comprehensive reports have appeared in recent literature on the utility and accuracy of DF and HF/DF methods over the traditionally used *ab initio* (HF and post-HF) approaches.[5,16,18] However, in spite of the availability of a large quantity of experimental data on vibrational spectra of transient species, such as, triplet state, radicals, etc. (from resonance Raman and infrared experiments), of a number of polyatomic systems, application of DFT methods for the prediction of vibrational frequencies and normal modes of transient species is scant (*vide infra*). In this paper, we have undertaken a comprehensive study of various DFT methods with particular emphasis on the structure and vibrational spectra for the excited state intermediates of *p*-benzoquinone (BQ), for which considerable experimental data are available.

p-Benzoquinone (BQ) and its reactive intermediates, such as triplet (T_1), semiquinone radical ($BQH^{\bullet}$), and semiquinone radical anion ($BQ^{\bullet-}$) constitute model systems for an important class of species involved in electron transport in biological systems.[19−21] These species have received much attention over the past 3 decades and still remain a major subject of growing interest in physical chemistry. In general, diffraction experiments by X-ray, electron, and neutron sources have been extensively used to obtain structural parameters of molecules in the ground state. However, for the transient species, there are no such direct experimental methods by which one can get the structural parameters. Resonance Raman (RR) and IR spectroscopic studies of various transient species have been proved to be very useful in providing valuable information regarding the structural changes involved. This has been accomplished by the comparison of the vibrational frequencies of the transient species (particularly in the structure sensitive region of 1300−1700 cm^{-1}) with those of the ground state.

The molecular and electronic structures of ground state BQ have been studied extensively in the past by both experimental[22,23] and theoretical[11,12,24−27] methods. Its vibrational frequencies observed in IR and Raman spectra have been assigned with the help of empirical and *ab initio* force field calculations as well as isotopic substitution experiments.[11,12,24−36] The structural, electronic, and vibrational properties of its semiquinone radical anion have also been studied by various methods, including resonance Raman,[37−45] IR,[46,47] ESR,[48,49] and electronic absorption[50] techniques and *ab initio* calculations.[24,39,40,51,52] Tripathi *et al.*[37−41] have reported the RR spectrum of this radical anion. Their experimental results on the vibrational frequencies were supported by theoretical calculations.[24,39,40] In separate studies the RR spectrum of this radical anion was reported by Beck and Brus[42,43] and also by Hester and Williams.[45] Beck and Brus[42,43] and Tripathi and Schuler[53] reported RR spectrum of the *p*-benzosemiquinone radical. The RR bands observed were assigned with the help of isotopic substitution experiments. A comparison of the vibrational frequencies observed for this radical with those for the corresponding radical anion showed that protonation of the oxygen atom has relatively little effect on the electronic structure of the semiquinone system.[53] Rossetti *et al.*[44] have studied the π^* antibonding distribution in the first

---

* Author to whom correspondence to be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1997.

S1089-5639(97)00159-X CCC: $14.00

excited triplet state (T_1) of BQ using the resonance Raman technique. The assignment of the RR bands observed was given on the basis of comparison with the results obtained for the semiquinone radical anion and from the isotopic shifts observed for the perdeuterated species. All of these experimental and theoretical studies have led to a detailed understanding of various properties of the transients but lack information on normal mode descriptions. An accurate assignment of the experimental frequencies of transients to vibrational modes requires various approaches such as investigations of isotopic shifts and normal mode calculations.

Quantum mechanical calculations have been successfully applied in the past for assigning the experimental vibrational frequencies of ground state as well as transient species.[1−18,24−27,39,40,54−68] Among the various methods used, recent studies on the ground state molecules of similar systems[11−14,63,64] indicate that DF and hybrid HF/DF methods (which are computationally less demanding than MP2 and CI methods) give results which are in very good agreement with the experiment. Although these methods have been extensively used to calculate structure and vibrational spectra of molecules in the ground state,[1−18,63,64] such studies on transient intermediates are rather limited in the literature.[59−62,65−68] Keszthelyi *et al.*[59−61] have used DFT methods to calculate the vibrational spectra of radical cations of 1,3-butadiene and 1,3-pentadiene. Quin and Wheeler[62,66] have studied the structure, spin properties, and vibrational spectra of phenol radical cation and phenoxy radical using DFT methods. O'Malley and Collins[68] have successfully applied the B3LYP functional to calculate geometries and hyperfine coupling constants for *p*-benzosemiquinone, durosemiquinone, and plastosemiquinone radical anions.

In the present work, we have carried out quantum mechanical calculations on the structure and vibrational spectra of the benzoquinone triplet (T_1), $BQ^{\bullet -}$, and $BQH^{\bullet}$ using both HF and a variety of DF and hybrid HF/DF methods such as SVWN, BLYP, BP86, B3LYP, B3P86, and B3PW91. Calculations have also been performed on the ground state (S_0) in order to make a common basis for comparison. We have chosen the highly symmetric BQ (D_{2h} symmetry) which allows us to perform quantum mechanical calculations using relatively large basis sets and with the inclusion of electron correlation effects. The availability of a large amount of experimental results for the ground state as well as for the transient facilitates the comparison of the calculated values. To the best of our knowledge, this is the first report on the quantum mechanical calculations on the structure and vibrational spectra of the *p*-benzoquinone triplet and its semiquinone radical. The present studies are undertaken with the following objectives: (1) to check the reliability of the various DF and HF/DF methods in predicting the vibrational frequencies of the transient species of polyatomic systems, such as *p*-benzoquinone, (2) to assign the reported experimental frequencies of the transients using normal mode analysis, and (3) to systematically study the structural changes involved in the transient species by analyzing the calculated bond distances and bond orders.

Computational Methods

The Hartree−Fock (HF), density-functional (DF), and hybrid Hartree−Fock/density-functional (HF/DF) calculations[69−81] were performed with the Gaussian-94/DFT[82] program on an IBM RS-6000 computer system. The calculations for the ground state were carried out using the restricted Hartree−Fock (RHF) and closed shell DFT formalisms, whereas those for the triplet, semiquinone radical, and semiquinone radical anion were carried out using either the unrestricted Hartree−Fock (UHF) formalism or density-functional theory (DFT), employing open shell wave functions. The calculations were carried out employing both 6-31G(d) and 6-31G(d,p) basis sets. The exchange functional used in the various DFT calculations were the local spin density exchange functional of Slater (abbreviated as S)[71] and the gradient corrected functional of Becke (B).[72] The correlation functionals include the local density functional of Vosko, Wilk, and Nusair (VWN),[73] the gradient corrected functional of Perdew (P86),[74] the correlation functional of Lee, Yang, and Paar (LYP),[75,76] and the 1991 gradient corrected functional of Perdew and Wang (PW91).[77] The three parameter hybrid HF/DF methods used were B3LYP, B3P86, and B3PW91.[78−81] A complete geometry optimization was carried out in all cases employing Berny's optimization algorithm.[83] The bond orders were calculated at the optimized geometries using natural bond order (NBO) analysis. The vibrational frequencies and corresponding normal modes were evaluated for the optimized geometries using analytical differentiation algorithms contained within the program. The assignment of the calculated normal modes was made from the corresponding potential energy distributions (PEDs) and isotopic shifts. The PEDs and frequencies of the isotopically labeled species were calculated from the quantum mechanically derived Cartesian force field using MOLVIB program.[84] For the ground state, triplet state, and radical anion (all D_{2h} symmetry), a complete normal mode analysis was carried out using the MOLVIB program. Such a complete normal mode analysis was not performed for the semiquinone radical because of its lower symmetry (C_s). However, its normal modes were analyzed by transforming the calculated displacements from Cartesian to internal coordinate basis using a program, NMODES,[85] developed in our laboratory. In all cases assignments of the calculated frequencies were clarified by visual inspection of the normal modes using the program NMODES. The vibrational frequencies obtained using RHF and UHF methods were uniformly scaled by 0.89,[54] whereas those obtained using the DF and HF/DF methods are reported without scaling.

Results and Discussion

We first examine the geometrical structures of BQ and its semiquinone radical anion, triplet state, and semiquinone radical and then discuss the vibrational spectra, isotopic shifts, and assignments. The calculations using both 6-31G(d) and 6-31G(d,p) basis sets gave similar results. Hence, for the sake of brevity, only the results obtained by using the qualitatively superior 6-31G(d,p) basis set are presented here, and those obtained using 6-31G(d) basis sets are provided as Supporting Information.

Geometrical Structure. The definition of the geometrical parameters are shown in Figure 1. Optimized geometries of the ground state, triplet state, and radical anion correspond to D_{2h} symmetry (Figure 1a), whereas that of semiquinone radical corresponds to C_s symmetry (Figure 1b). In all cases $C_5{-}C_6$ and $C_2{-}C_3$ bonds are represented as C=C throughout the discussion irrespective of the bond distance values in order to distinguish these from the other set of C−C bonds $C_1{-}C_2$, $C_3{-}C_4$, $C_4{-}C_5$, and $C_1{-}C_6$.

Ground State S_0. The optimized structural parameters of BQ calculated by various methods are given in Table 1 along with the available values from the X-ray[22] and electron diffraction (ED)[23] experiments. The C=C bond distance obtained at the RHF level (1.323 Å) is underestimated compared to the ED value (1.344 Å), whereas it compares well with the X-ray diffraction value of 1.322 Å. The corresponding bond distance values obtained using SVWN, B3LYP, B3P86, and B3PW91

TABLE 1: Optimized Structural Parameters for *p*-Benzoquinone (BQ) As Obtained by Various Methods

structural param[a]	calculated using the 6-31G(d,p) basis set							expt	
	RHF	SVWN	BLYP	B3LYP	B3P86	B3PW91	BP86	X-ray	ED[c]
C=C	1.323	1.343	1.356	1.343	1.341	1.341	1.355	1.322	1.344
C=O	1.194	1.228	1.241	1.225	1.222	1.223	1.239	1.222	1.225
C−C	1.489	1.469	1.494	1.486	1.481	1.483	1.490	1.477	1.481
C−H	1.074	1.096	1.093	1.086	1.086	1.087	1.095		1.089
C=C−C	121.4	121.1	121.4	121.4	121.3	121.3	121.3	121.1	121.0
C−C=O	121.4	121.1	121.4	121.4	121.3	121.3	121.3	121.1	121.0
C−C−C	117.2	117.7	117.2	117.2	117.4	117.3	117.3	117.8	118.1
C−C−H	115.8	115.7	115.9	115.8	115.9	115.9	115.9		

[a] Bond lengths in angstroms and bond angles in degrees. [b] X-ray diffraction values from ref 22. [c] Electron diffraction values from ref 23.

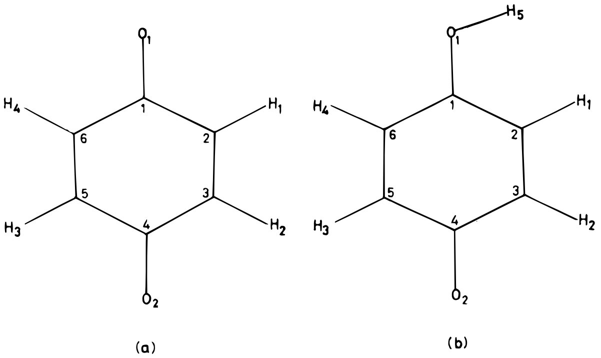


Figure 1. Numbering of the atoms of (a) benzoquinone (S_0), benzosemiquinone radical anion ($BQ^{\bullet-}$), and benzoquinone triplet (T_1) and (b) benzosemiquinone radical ($BQH^{\bullet}$).

TABLE 2: Optimized Structural Parameters for *p*-Benzosemiquinone Radical Anion ($BQ^{\bullet-}$) As Obtained by Various Methods

structural param[a]	calculated using the 6-31G(d,p) basis set						
	UHF	SVWN	BLYP	B3LYP	B3P86	B3PW91	BP86
C=C	1.356	1.368	1.383	1.372	1.369	1.370	1.382
C=O	1.245	1.263	1.280	1.266	1.263	1.264	1.277
C−C	1.444	1.444	1.465	1.453	1.449	1.450	1.459
C−H	1.078	1.099	1.097	1.089	1.089	1.089	1.099
C=C−C	122.7	122.7	122.7	122.7	122.7	122.7	122.8
C−C=O	122.7	122.7	122.7	122.7	122.7	122.7	122.8
C−C−C	114.7	114.6	114.5	114.6	114.5	114.5	114.4
C−C−H	116.5	115.7	116.1	116.2	116.2	116.2	116.1

[a] Bond lengths in angstroms and bond angles in degrees.

methods (1.343, 1.343, 1.341, and 1.341 Å, respectively) are in good agreement with the experimental value of 1.344 Å. However, the other two methods (BLYP and BP86) are found to overestimate the C=C bond distance by 0.012 and 0.011 Å, respectively. A similar trend is also seen in the case of the C=O bond distance, whereas the calculated C−C bond distances show a slightly different trend. The RHF, B3LYP, B3P86, and B3PW91 methods yield C−C bond distances (1.489, 1.486, 1.481, and 1.483 Å, respectively) which are close to the experimental value of 1.481 Å (ED).[23] The SVWN method is found to underestimate it by 0.012 Å, whereas BLYP and BP86 methods overestimate it by 0.013 and 0.009 Å, respectively. For the C−H bond distances, only the hybrid HF/DF methods (B3LYP, B3P86, and B3PW91) yield results in agreement with the experimental value of 1.089 Å. As can be seen from the table, the bond angles calculated using all of the methods are in good agreement with the experimental results. Therefore, a comparison of the calculated structural parameters with the corresponding experimental values show that the RHF method is not good enough to predict the structural parameters of BQ, particularly the C=C and C=O bond distances. The SVWN method gives C=C and C=O bond distances in good agreement with the experimental values. However, the other bond distances (C−C and C−H) are not reproduced. The BLYP and BP86 methods overestimate all of the bond distances. The structural parameters calculated using the hybrid HF/DF methods B3LYP, B3P86, and B3PW91 are found to be close to each other. As can be seen from the table and also as reported earlier by Boesch and Wheeler,[11] the best results for the structural parameters are obtained by using these hybrid HF/DF methods.

Radical Anion $BQ^{\bullet-}$. The optimized structural parameters for the benzosemiquinone radical anion using various methods are listed in Table 2. Although the calculated bond distance values vary from one method to another, the trend in variation is found to be similar to that observed for the ground state. As seen for the ground state (Table 1), the bond distances calculated using the three HF/DF methods B3LYP, B3P86, and B3PW91 are close to each other. Except for the C−H bond distance, the structural parameters calculated using the SVWN method are comparable to those obtained using these HF/DF methods. The corresponding UHF values are lower, whereas the BLYP and BP86 calculations give bond distance values which are greater than those obtained using the other methods. The bond angles calculated using all of the methods are found to be close to each other. However, from this calculation of the structural parameters it is not possible to assess the superiority of one method over the other methods in predicting the geometrical structure of the radical anion because of the lack of experimental values for a direct comparison. However, the structural differences seen for the radical anion in comparison with the ground state are found to follow a pattern similar to that reported earlier by Chipman and Prebenda[24] in their UHF calculations performed using the 3-21G basis set. The calculated electronic state of $^2B_{2g}$ for the radical anion shows that the singly occupied orbital is the b_{2g} antibonding π^* orbital. As reported earlier,[24] this b_{2g} orbital is antibonding with respect to C=C and C=O bonds and bonding with respect to the C−C bonds, implying that the C=C and C=O bonds should be elongated and C−C bonds should be contracted for the radical anion in comparison with those for the ground state. The structural parameters calculated using all of the methods (Table 2) clearly show this trend. For example, the C=C, C=O, and C−C bond distances calculated using the B3LYP method are 1.372, 1.266, and 1.453 Å, respectively. A comparison with the corresponding values for the ground state (Table 1) shows that the C=C and C=O bonds are elongated by 0.029 and 0.041 Å, respectively. The C−C bond is shortened by 0.033 Å. As shown in Figure 2, the corresponding bond order values are consistent with these changes in the structural parameters. Overall, the best method for optimization of radical anion structure, perhaps, should be decided from the frequency calculation (*vide infra*).

Triplet State T_1. Geometry optimization of the lowest triplet state of *p*-benzoquinone (T_1) by various methods gives a planar structure with D_{2h} symmetry. The corresponding optimized structural parameters are listed in Table 3. The variation in

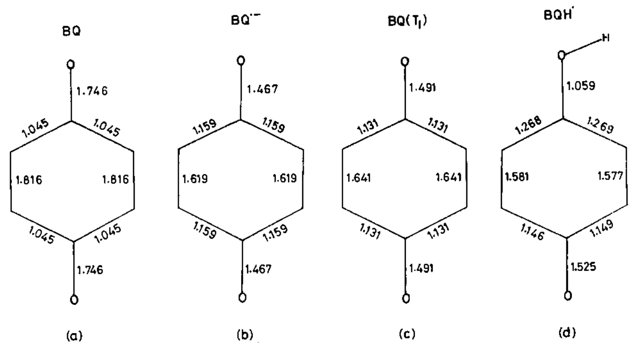


Figure 2. Bond orders of BQ (S_0), $BQ^{\bullet -}$ BQ (T_1), and $BQH^{\bullet}$ obtained using B3LYP calculation.

TABLE 3: Optimized Structural Parameters for the *p*-Benzoquinone Triplet (T_1) As Obtained by Various Methods

structural param[a]	calculated using the 6-31G(d,p) basis set						
	UHF	SVWN	BLYP	B3LYP	B3P86	B3PW91	BP86
C=C	1.338	1.353	1.368	1.356	1.353	1.354	1.366
C=O	1.231	1.253	1.274	1.257	1.252	1.253	1.269
C−C	1.454	1.445	1.464	1.456	1.452	1.453	1.464
C−H	1.072	1.093	1.090	1.083	1.083	1.084	1.092
C=C−C	121.9	122.2	122.0	122.0	122.1	122.1	122.1
C−C=O	121.9	122.2	122.0	122.0	122.1	122.1	122.1
C−C−C	116.1	115.5	116.1	115.9	115.8	115.8	115.8
C−C−H	116.3	116.0	116.5	116.3	116.3	116.3	116.4

[a] Bond lengths in angstroms and bond angles in degrees.

the calculated bond distances from one method to another shows a trend very similar to that observed in the case of the ground state and the radical anion. The C=C bond distance values calculated using SVWN, B3LYP, B3P86, and B3PW91 (1.353, 1.356, 1.353, and 1.354 Å) are close to each other. But the UHF method predicts a shorter (1.338 Å) and the other two methods BLYP and BP86 predict longer (1.368 and 1.366 Å) C=C bonds. A similar trend is seen in the case of C=O bond distance also. The C−C bond distance obtained using the UHF method (1.454 Å) is closer to those obtained using B3LYP, B3P86, and B3PW91 methods (1.456, 1.452, and 1.453 Å, respectively), whereas the SVWN method gives a slightly shorter C−C bond (1.445 Å). The BLYP and BP86 methods yield C−C bonds (both 1.464 Å) which are longer than those obtained using the other methods. As seen from the table, the bond angles calculated using various methods do not show any significant variation from one method to another. However, as can be noticed from Tables 1 and 3, the structural parameters show significant changes on excitation from the ground state to the triplet state. Since the trend in this variation is similar for all of the methods, for the sake of brevity, only the structural parameters obtained at the B3LYP method are used for discussion. The C=C bonds of the triplet state show significant elongation (by 0.013 Å) compared to those for the ground state. The calculated C=C bond distance (1.356 Å) and bond order (1.641) values show considerable reduction in the corresponding bond strength. The C=O bond distance value has also significantly increased (by 0.032 Å) on excitation to the triplet state. Thus, it is apparent that the increase in the C=O bond distance is more than that seen for the C=C bond. Further, the C−C bonds of the triplet state are shorter (by 0.030 Å) than those of the ground state. As shown in Figure 2c, the corresponding bond orders are consistent with these variations in the bond distances. Therefore, we find that in the triplet state, the structure of the molecule is elongated along the C=O axis (vertically) and compressed in the perpendicular direction. This is also evidenced from the increase of C=C−C and C−C=O bond angles and decrease of C−C−C bond angle as seen from Tables 1 and 3. These structural changes seen for the triplet in comparison with the ground state can also be explained from the calculated electronic structure as follows.

The lowest excited triplet state (T_1) is often considered as similar to the corresponding radical anion, since in both species the same antibonding π^* orbital (in this case the b_{2g} orbital) is populated. The calculation shows that the T_1 of BQ, with an electronic state of $^3B_{1g}$, corresponds to an n-π^* excitation of an electron from the b_{3g} orbital (HOMO of BQ) to the antibonding π^* orbital b_{2g} (LUMO of BQ). Hence, the singly occupied orbitals are b_{3g} and b_{2g}. The spin contamination due to the use of unrestricted open shell methodology was found to be very low, with the maximum deviation not exceeding 0.05 compared to the actual value of $S(S + 1) = 2$ for a triplet state. This shows that the calculated wave functions represent the triplet state with negligible contamination from the other multiplets. Therefore, population of the b_{2g} orbital (π^*), which is antibonding with respect to C=C and C=O bonds and bonding with respect to C−C bonds, should result in weakening of C=C and C=O bonds and strengthening of the C−C bonds. This is reflected in the calculated bond lengths and corresponding bond orders for the triplet state. A comparison of the calculated bond orders of the triplet state with those for the ground state and radical anion is summarized in Figure 2. As shown in the figure, the C=C and C=O bonds show weakening on going from the ground state to the triplet one and then to the radical anion ($S_0 > T_1 > BQ.^{-}$), whereas the C−C bonds show the opposite trend ($S_0 < T_1 < BQ^{\bullet -}$). The elongation of the C=O bond to a greater extent than the C=C bond is consistent with the n-π^* nature of the lowest triplet state. The calculated (using B3LYP) atomic spin densities are found to be 0.122, 0.117, and 0.612 for C ($C_2{=}C_3$ and $C_5{=}C_6$), C ($C_1{=}O_1$ and $C_4{=}O_2$), and O atoms, respectively. The higher value for the unpaired spin density in the carbonyl part of the triplet species also supports the large increase in the C=O bond distance. These changes in the structural parameters supported by the bond orders and spin densities show that the triplet state is intermediate between the ground state and the radical anion.

Semiquinone Radical $BQH^{\bullet}$. Geometry optimization of the semiquinone radical was performed by starting with the triplet structure in which one hydrogen atom was attached to one of the oxygen atoms. For all of the methods, the optimization showed that the minimum in the potential energy surface corresponds to a planar structure with C_s symmetry as represented in Figure 1b. The optimized structural parameters for this semiquinone radical obtained by using various methods are given in Table 4. The corresponding bond angles are not included in the table for the sake of brevity. Since the trend seen in the variation of the calculated bond distances from one method to another is similar, only the bond distances and bond orders (Figure 2) obtained using the B3LYP method are used for the discussion. The $C_2{-}C_3$ and $C_5{-}C_6$ bond distances are found to be 1.375 and 1.373 Å, respectively. This shows that these bonds are elongated by 0.032 and 0.030 Å, respectively, in comparison with that of the ground state. The $C_4{-}O_2$ and $C_1{-}O_1$ bond distances are 1.256 and 1.354 Å, respectively. In comparison with the ground state, the former shows an elongation of 0.031 Å, whereas the latter show an elongation of 0.129 Å which is large enough to make it close to a single bond. The $C_1{-}C_2$ and $C_1{-}C_6$ bonds (both 1.413 Å) are shortened by 0.073 Å, and the $C_3{-}C_4$ and $C_4{-}C_5$ bonds (both 1.454 Å) are shortened by 0.032 Å with respect to the ground state. Hence, the C−C bonds adjacent to the −OH group are shortened to a greater extent than the other two. A long C_1-

TABLE 4: Optimized Structural Parameters of *p*-Benzosemiquinone Radical (BQH•) As Obtained by Various Methods

structural param[a]	calculated using the 6-31G(d,p) basis set						
	UHF	SVWN	BLYP	B3LYP	B3P86	B3PW91	BP86
C_2-C_3	1.385	1.369	1.384	1.375	1.372	1.373	1.383
C_5-C_6	1.382	1.368	1.383	1.373	1.370	1.371	1.381
C_4-O_2	1.253	1.251	1.267	1.256	1.252	1.253	1.264
C_1-O_1	1.350	1.339	1.369	1.354	1.347	1.348	1.362
C_1-C_2	1.405	1.407	1.423	1.413	1.410	1.412	1.422
C_1-C_6	1.408	1.407	1.424	1.413	1.411	1.412	1.422
C_3-C_4	1.439	1.446	1.466	1.454	1.449	1.451	1.463
C_4-C_5	1.439	1.446	1.467	1.454	1.449	1.451	1.463
C_2-H_1	1.077	1.099	1.096	1.089	1.088	1.089	1.098
C_3-H_2	1.074	1.095	1.092	1.085	1.085	1.085	1.094
C_5-H_3	1.074	1.095	1.092	1.085	1.085	1.085	1.094
C_6-H_4	1.074	1.095	1.092	1.085	1.085	1.085	1.094
O_1-H_5	0.943	0.978	0.979	0.967	0.965	0.965	0.078

[a] Bond lengths are given in angstroms; for a definition of parameters, see Figure 1b.

O_1 bond (1.354 Å) and short C_1-C_2 and C_1-C_6 bonds (1.413 Å) imply that the structure of this part of the semiquinone radical is close to that of phenol, whereas the other part resembles the radical anion. The calculated bond orders listed in Figure 2d show the nature of each bond. The trend in these bond order values is found to be consistent with that seen for the corresponding bond distances. Hence, the calculated bond distances and corresponding bond order values imply that the structure of the semiquinone radical is much different from the symmetrical quinonoid structure seen in the case of the triplet and radical anion.

Vibrational Frequencies and Assignments. The assignments of the calculated vibrational frequencies of BQ and its transients, based on normal mode analysis, isotopic shifts, and a comparison with the reported experimental results, are provided in the following sections. Since the isotopic shifts calculated using the BP86 method were found to be closer to experimental data than the results obtained using the other methods, only the PEDs and isotopic shifts from the BP86 calculations are discussed in detail. However, the vibrational frequencies calculated using all of the methods are compared with experimental data.

Ground State S_0. The symmetries, vibrational frequencies, isotopic shifts (for the perdeuterated derivative), PEDs, and approximate descriptions for the in-plane normal modes of BQ calculated at the BP86/6-31G(d,p) level are given in Table 5. The experimental frequencies and isotopic shifts from the literature[31,35,36] are also included in the table for comparison. As reported earlier by Nonella and Tavan,[12] the vibrational frequencies calculated using the BP86/6-31G(d,p) method are close to the experimental values, particularly in the 1300−1700 cm^{-1} region (Figure 3a). The calculated d_4 isotopic shifts are also found to be in excellent agreement with the corresponding experimental values. These shifts are also consistent with the PEDs and assignments of the normal modes. This force field was earlier shown to reproduce the experimental isotopic shifts of ^{13}C and ^{18}O labeled derivatives of BQ.[12] The calculated normal mode compositions and isotopic shifts are also found to be consistent with the scaled quantum mechanical (SQM) results of Liu *et al*.[25] The normal mode descriptions and isotopic shifts obtained using the other DFT methods were found to be similar, which are not included in the discussion for the sake of brevity. We would like to note that the RHF calculation results in different mode compositions, and therefore the isotopic shifts deviate considerably from the experimental values. A comparison of the vibrational frequencies calculated using the various methods is given in Table 6. As mentioned earlier, the values obtained at the RHF level are scaled by a uniform factor of 0.89. Even after scaling, in comparison with the experiment, the RHF frequencies are overestimated in the structure sensitive region of 1300−1700 cm^{-1} but are comparable to the experimental values at low frequencies. The vibrational frequency values calculated using the BLYP and BP86 methods are close to each other and show good agreement with the experiment without any scaling, particularly in the structure sensitive region. But for many normal modes in the low-frequency side, the calculated frequency values using these two methods are less than the corresponding experimental values. The frequencies calculated using the three HF/DF methods are found to be very similar. The SVWN method predicts frequency values which are intermediate between those obtained using the HF/DF methods and BP86 method. As can be seen from the table, the

TABLE 5: Symmetries, Frequencies, d_4 Isotopic Shifts, PEDs, and Approximate Descriptions for the In-Plane Normal Modes of *p*-Benzoquinone (BQ)

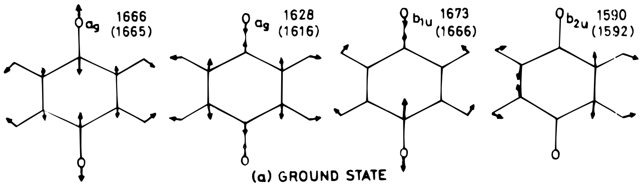
sym	freq[a]		d_4 shift[a,b]		PED[c] (%)	approx description
	BP86	expt[d]	BP86	expt[d]		
a_g	3131	3063	797	774	C−H(99)	C−H stretch
	1666	1665	11	12	C=O(56), C=C(20), δCH(10)	C=O stretch
	1628	1616	30	27	C=C(59), C=O(21), δCH(14)	C=C stretch
	1126	1149	312	320	δCH(92)	C−H bend
	759	771	24	26	C−C(65), δCCC(18)	ring breath
	441	443	5	5	δCCC(79)	ring bend
b_{3g}	3112	3046	812	769	C−H(99)	C−H stretch
	1353	1394	66	54	C−C(52), δCH(33)	C−C stretch
	1192	1234	214	309	δCH(56), C−C(28)	C−H bend
	581	599	22	17	δCCC(47), δCO(22), C−C(21)	ring bend
	433	482	28	20	δCO(52), δCCC(23)	C=O bend
b_{1u}	3111	3062	811	785	C−H(99)	C−H stretch
	1673	1666	5	6	C=O(89)	C=O stretch
	1338	1354	193	194	δCH(82), δCCC(10)	C−H bend
	917	944	73	71	δCCC(69), δCH(18)	ring bend
	734	728	86	93	C−C(72), δCCC(13)	C−C stretch
b_{2u}	3129	3062	798	785	C−H(99)	C−H stretch
	1590	1592	31	32	C=C(81), δCH(12)	C=C stretch
	1282	1299	59	51	C−C(67), δCH(25)	C−C stretch
	1048	1066	267	273	δCH(58), C−C(24)	C−H bend
	395	409	5	7	δCO(77), δCCC(12)	C=O bend

[a] Frequencies and isotopic shifts are in cm^{-1}. [b] Isotopic shift is for the perdeuterated derivative. [c] Calculated using the BP86/6-31G(d,p) force field. [d] Experimental values from refs 31, 35, and 36.

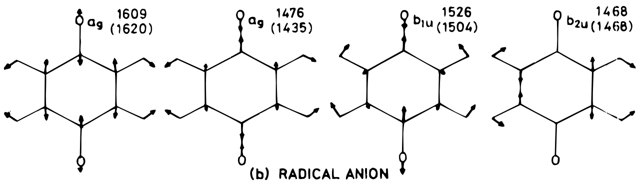
TABLE 6: Symmetries, Frequencies, and Approximate Descriptions for the In-Plane Normal Modes of *p*-Benzoquinone (BQ) As Obtained by Various Methods

	frequency (cm^{-1})								approx
sym	RHF[a]	SVWN	BLYP	B3LYP	B3P86	B3PW91	BP86	expt[b]	description
a$_g$	3021	3144	3129	3212	3231	3227	3131	3063	C−H stretch
	1797	1724	1647	1756	1777	1774	1666	1665	C=O stretch
	1652	1676	1615	1692	1707	1704	1628	1616	C=C stretch
	1121	1106	1135	1167	1161	1163	1126	1149	C−H bend
	731	793	749	776	787	784	759	771	ring breath
	430	445	443	455	454	453	441	443	ring bend
b$_{3g}$	3004	3125	3109	3293	3212	3208	3112	3046	C−H stretch
	1362	1378	1351	1402	1408	1406	1353	1394	C−C stretch
	1189	1198	1191	1235	1238	1236	1192	1234	C−H bend
	576	593	581	601	603	602	581	599	ring bend
	434	428	441	453	446	447	433	482	C=O bend
b$_{1u}$	3004	3125	3109	3193	3212	3207	3111	3062	C−H stretch
	1780	1734	1653	1758	1779	1776	1673	1666	C=O stretch
	1337	1328	1348	1388	1383	1383	1338	1354	C−H bend
	913	925	917	948	949	947	917	944	ring bend
	718	751	729	755	760	759	734	728	C−C stretch
b$_{2u}$	3020	3141	3126	3209	3229	3225	3129	3062	C−H stretch
	1631	1638	1579	1657	1673	1670	1590	1592	C=C stretch
	1275	1317	1273	1323	1334	1330	1282	1299	C−C stretch
	1046	1042	1050	1086	1085	1086	1048	1066	C−H bend
	400	402	396	411	412	412	395	409	C=O bend

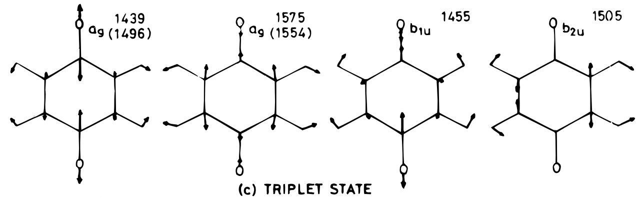
[a] RHF values are uniformly scaled by 0.89. [b] Experimental values from refs 31, 35, and 36.



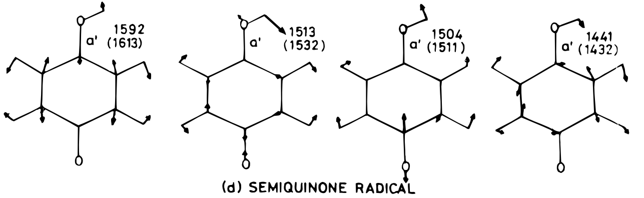
(a) GROUND STATE



(b) RADICAL ANION



(c) TRIPLET STATE



(d) SEMIQUINONE RADICAL

Figure 3. Calculated atomic displacements of normal modes involving C=C and C=O stretching motions of BQ and its transient intermediates. Symmetries, frequencies (cm^{-1}) calculated by using the BP86 method, and experimental frequencies (in parentheses) are also given. The scale for the displacements is arbitrary but common to all of the modes.

SVWN, B3LYP, B3P86, and B3PW91 frequencies are overestimated compared to the experimental values. The average error is found to be 2−4%. Considering the fact that these calculated frequencies are unscaled and harmonic in nature and the comparison is made with the experimental frequencies which involve anharmonicity, solvent effect, etc., overall the DF method SVWN and HF/DF methods B3LYP, B3P86, and B3PW91 yield the best results in terms of frequencies and geometries. However, in cases where little is known about the anharmonicity and other effects, the BLYP and BP86 methods can be used to predict the vibrational frequencies and normal mode descriptions, particularly in the structure sensitive region, albeit the geometrical structural predictions are not so accurate.

Radical Anion BQ$^{\bullet-}$. In Table 7 are listed the symmetries, vibrational frequencies, PEDs, isotopic shifts, and assignments for the in-plane normal modes of the benzosemiquinone radical anion obtained at the BP86/6-31G(d,p) level. The available experimental values for the frequencies and isotopic shifts[41,45,47] are also included in the table for comparison. Tripathi *et al.*[36−41] reported seven bands at 481, 831, 1161, 1271, 1435, 1472, and 1620 cm^{-1} in the RR spectrum of the anion radical. Of these, the 481, 831, 1161, 1435, and 1620 cm^{-1} bands were assigned to the totally symmetric (a$_g$) modes of the ring bend, ring breath, C−H bend, C=O stretch, and C=C stretch, respectively, and the bands at 1271 and 1472 cm^{-1} were assigned to b$_{3g}$ fundamentals of the C−H bend and C−C stretch, respectively. These assignments were further confirmed with the help of *ab initio* calculations.[24,39,40] The RR bands observed for the radical anion by Hester and Williams[45] at 484, 826, 1160, 1434, and 1619 cm^{-1} and those observed by Beck and Brus[42,43] at 1163, 1438, and 1622 cm^{-1} were also assigned in a similar way. Hester and Williams[45] reported two weak bands at 670 and 966 cm^{-1}, which they have assigned to ring bend and C−C stretch/C=O bend fundamentals, respectively. The calculated value of 608 cm^{-1} for the ring bend mode (b$_{3g}$ symmetry) supports the assignment of the first band. However, the present calculation does not give an a$_g$ or b$_{3g}$ fundamental which could be correlated to the second band. Hence, this 966 cm^{-1} band may be reassigned to the overtone of the ring bend (a$_g$) mode as 2 × 484. In an IR spectroscopic study of the radical anion, Bauscher and Mantele[47] reported two bands at 1504 and 1468 cm^{-1}. The present calculation gives asymmetric C=O (b$_{1u}$) and C=C (b$_{2u}$) stretching fundamentals 1526 and 1468 cm^{-1}. Hence, the bands observed at 1504 and 1468 cm^{-1} could be easily assigned to the asymmetric C=O and C=C stretching fundamentals (as shown in Figure 3b). As seen from Table 7, the excellent agreement between the calculated and experimental frequencies as well as d$_4$ isotopic shifts supports the assignment of the bands and shows the reliability of the BP86/6-31G(d,p) force field for predicting the vibrational frequencies and normal mode

TABLE 7: Symmetries, Frequencies, d$_4$ Isotopic Shifts, PEDs, and Approximate Descriptions for the In-Plane Normal Modes of *p*-Benzosemiquinone Radical Anion ($BQ^{\bullet -}$)

sym	frequency[a]		d$_4$ shift[a,b]		PED[c] (%)	approx description
	BP86	expt[d]	BP86	expt[d]		
a$_g$	3069				C−H(99)	C−H stretch
	1609	1620 (1619)[e]	24	23	C=(66), C=O(16), δCH(12)	C=C stretch
	1476	1435 (1434)	9	9	C=O(62), C=C(20), δCH(11)	C=O stretch
	1111	1161 (1160)	309	317	δCH(87)	C−H bend
	798	831 (826)			C−C(76), δCCC(14)	ring breath
	452	481 (484)	4	1	δCCC(59), C−C(17)	ring bend
b$_{3g}$	3038				C−H(99)	C−H stretch
	1402	1472	41	79	C−C(68), δCH(18)	C−C stretch
	1207	1271	235	251	δCH(59), C−C(21)	C−H bend
	608	(670)			δCCC(63), δCO(18), C−C(15)	ring bend
	448				δCO(78), δCCC(13)	C=O bend
b$_{1u}$	3039				C−H(99)	C−H stretch
	1526	1504[f]			C=O (82)	C=O stretch
	1329				δCH(75), δCCC(14)	C−H bend
	930				δCCC(68), δCH(13), C−C(11)	ring bend
	764				C−C(77), δCCC(18)	C−C stretch
b$_{2u}$	3061				C−H(99)	C−H stretch
	1468	1468[f]			C=C(78), δCH(14)	C=C stretch
	1204				C−C(59), δCH(31)	C−C stretch
	1034				δCH(61), C−C(28)	C−H bend
	375				δCO(81), δCCC(12)	C=O bend

[a] Frequencies and isotopic shifts are in cm^{-1}. [b] Isotopic shift is for the perdeuterated derivative. [c] Calculated using the BP86/6-31G(d,p) force field. [d] Experimental values of Tripathi *et al.*[41] [e] Experimental values in parentheses are of Hester and Williams.[45] [f] Experimental values of Bauscher and Mantele.[47]

TABLE 8: Symmetries, Frequencies, and Approximate Descriptions for the In-Plane Normal Modes of *p*-Benzosemiquinone Radical Anion ($BQ^{\bullet -}$) As Obtained by Various Methods

sym	frequency (cm^{-1})								approx description
	UHF[a]	SVWN	BLYP	B3LYP	B3P86	B3PW91	BP86	expt[b]	
a$_g$	1643	1668	1593	1671	1690	1686	1609	1620	C=C stretch
	1479	1540	1455	1526	1547	1543	1476	1435	C=O stretch
	1110	1090	1120	1151	1146	1147	1111	1161	C−H bend
	787	827	790	822	831	829	798	831	ring breath
	449	456	455	469	468	467	452	481	ring bend
b$_{3g}$	1431	1439	1394	1457	1469	1466	1402	1472	C−C stretch
	1217	1198	1214	1256	1253	1253	1207	1271	C−H bend
	609	617	609	631	632	631	608	670	ring bend
b$_{1u}$	1497	1594	1504	1571	1595	1589	1526	1504	C=O stretch
b$_{2u}$	1451	1514	1459	1517	1529	1526	1468	1468	C=C stretch

[a] UHF values are uniformly scaled by 0.89. [b] Experimental values from refs 41, 45, and 47.

descriptions of such systems. As seen earlier in the case of ground state, isotopic shifts and normal mode descriptions calculated for the radical anion using other DFT methods are found to be similar to those obtained using the BP86 method. A comparison of the vibrational frequencies of the radical anion calculated using the various methods with the corresponding experimental values are summarized in Table 8. Only the normal modes for which experimental frequencies are available are included in the table. As seen from the table, the variation of the calculated frequencies from one method to another follows a trend similar to that seen earlier for the ground state. The totally symmetric C=C and C=O stretching frequencies are reproduced well in BLYP and BP86 calculations. The other methods SVWN, B3LYP, B3P86, and B3PW91 are found to slightly overestimate these frequencies, but in the lower frequency side they show better agreement with experiment. The calculated IR intensities of the asymmetric C=O stretching mode (b$_{1u}$) are 405, 321, 265, 301, 323, 317, and 287 km/mol, respectively for UHF, SVWN, BLYP, B3LYP, B3P86, B3PW91, and BP86 methods. For the asymmetric C=C stretching mode (b$_{2u}$) the corresponding values are 98, 27, 32, 43, 43, 44, and 31 km/mol, respectively. This shows that the IR intensity of the C=O stretching (b$_{1u}$) mode is 5−12 times more than that of the C=C stretching (b$_{2u}$) mode. However, the exact comparison of these calculated intensities is not possible because of the nonavailability of experimental data for the radical anion.

Triplet State T$_1$. The symmetries, vibrational frequencies, PEDs, d$_4$ isotopic shifts, and approximate descriptions for the in-plane normal modes of the triplet state (T$_1$) calculated using the BP86 method are listed in Table 9 along with the experimental values reported in the literature.[44] A comparison of the PEDs calculated for T$_1$ in-plane normal modes with those of S$_0$ shows that the mode descriptions are similar. The only noticeable difference is the reversal in the ordering of the totally symmetric C=O and C=C stretching fundamentals. Rossetti *et al.*[44] reported RR bands at 455, 901, 947, 1163, 1360, 1496, 1554, and 2003 cm^{-1} for the T$_1$ state of BQ in water. Of these, the bands at 1554 and 1496 cm^{-1} were assigned[44] to C=C and C=O stretching fundamentals, respectively, based on the isotopic shifts observed for its perdeuterated counterpart and also using the information obtained from the low-temperature $T_1 \leftarrow S_0$ absorption studies. The present calculation gives a normal mode at 1575 cm^{-1} with a major contribution from C=C stretching and one at 1439 cm^{-1} with significant contribution from C=O stretching (as shown in Figure 3c). This is in agreement with the assignment of these bands given by Rossetti *et al.*[44] The calculated d$_4$ isotopic shift of 29 cm^{-1} for the 1575 cm^{-1} mode compares well with the experimental value of 25

TABLE 9: Symmetries, Frequencies, d_4 Isotopic Shifts, PEDs, and Approximate Descriptions for the In-Plane Normal Modes of *p*-Benzoquinone Triplet (T_1)

	frequency^{a}		d_4 shift^{a,b}			
sym	BP86	expt^{d}	BP86	expt^{d}	PED^{c} (%)	approx description
a_g	3153				C−H(99)	C−H stretch
	1575	1554	29	25	C═C(59), C═O(13), δCH(15)	C═C stretch
	1439	1496			C═O(65), C═C(14), δCH(10)	C═O stretch
	1151	1163	323	320	δCH(90)	C−H bend
	795				C−C(79), δCCC(12)	ring breath
	428	455	4	2	δCCC(67), C−C(23)	ring bend
b_{3g}	3137				C−H(99)	C−H stretch
	1326	1360			C−C(56), δCH(29)	C−C stretch
	1211				δCH(53), C−C(30)	C−H bend
	599				δCCC(49), δCO(28), C−C(12)	ring bend
	453				δCO(75), δCCC(21)	C═O bend
b_{1u}	3135				C−H(99)	C−H stretch
	1455				C═O(90)	C═O stretch
	1324				δCH(86), δCCC(11)	C−H bend
	920				δCCC(49), δCH(16), C−C(14)	ring bend
	738				C−C(58), δCCC(27)	C−C stretch
b_{2u}	3151				C−H(99)	C−H stretch
	1505				C═C(63), δCH(16)	C═C stretch
	1189				C−C(60), δCH(29)	C−C stretch
	1025				δCH(52), C−C(27)	C−H bend
	371				δCO(80), δCCC(14)	C═O bend

[a] Frequencies and isotopic shifts are in cm^{-1}. [b] Isotopic shift is for the perdeuterated derivative. [c] Calculated using the BP86/6-31G(d,p) force field. [d] Experimental values of Rossetti *et al.*[44]

TABLE 10: Symmetries, Frequencies, and Approximate Descriptions for the In-Plane Normal Modes of *p*-Benzoquinone Triplet (T_1) As Obtained by Various Methods

	frequency (cm^{-1})								
sym	UHF^{a}	SVWN	BLYP	B3LYP	B3P86	B3PW91	BP86	expt^{b}	approx description
a_g	1577	1623	1563	1627	1642	1638	1575	1554	C═C stretch
	1396	1523	1408	1480	1509	1504	1439	1496	C═O stretch
	1144	1132	1160	1190	1185	1186	1151	1163	C−H bend
	762	822	788	813	822	819	795		ring breath
	420	428	433	443	440	439	428	455	ring bend
b_{3g}	1333	1340	1331	1374	1375	1373	1326	1360	C−C stretch

[a] UHF values are uniformly scaled by 0.89. [b] Experimental values of Rossetti *et al.*[44]

cm^{-1}. This clearly supports the assignment of this band to C═C stretching because deuteration on the ring is expected to show a significant shift in this frequency as seen in the case of the ground state. The band observed at 1163 cm^{-1} is undoubtedly the C−H in-plane bend. The calculated value of 1151 cm^{-1} for this mode compares well with the experimental value in addition to the excellent agreement between the calculated and experimental (323 against 320 cm^{-1}) d_4 isotopic shifts. The calculated in-plane ring bend at 428 cm^{-1} compares well with the experimental value of 455 cm^{-1}. None of the calculated totally symmetric (a_g) fundamental vibrational modes could be correlated to the weak band observed at 1360 cm^{-1}. One possibility is that it can be assigned to the C−C stretching fundamental of b_{3g} symmetry, since the calculation gives a b_{3g} mode at 1326 cm^{-1} with a major C−C stretching contribution. The band observed at 2003 cm^{-1} could be assigned to a combination band of 1554 (C═C stretch) and 455 (ring bend) cm^{-1}. The band observed at 901 cm^{-1} can be assigned to the first overtone of the ring bend as 2 × 455. However, there is no calculated a_g or b_{3g} frequency value which could be correlated to the band observed at 947 cm^{-1}. Also, the calculated frequency for the ring breath mode at 795 cm^{-1} has no experimental counterpart, but it is interesting to note that the ring breath fundamental in the ground state and radical anion are observed at 771 and 831 cm^{-1}, respectively.[36,41] In general, as observed in the case of the ground state and radical anion, the frequencies and isotopic shifts for the triplet state (T_1) calculated at the BP86/6-31(d,p) level are in good agreement with the experimental values. The isotopic shifts and normal mode descriptions obtained using other DF and HF/DF methods are found to be similar to those of BP86 calculations. The comparison of the frequencies calculated using the various methods are summarized in Table 10. The method to method variations in the calculated frequencies are found to be similar to those seen earlier for the ground state and radical anion. The BLYP and BP86 methods yield similar results. The frequencies calculated by the other methods SVWN, B3LYP, B3P86, and B3PW91 are comparable to each other and also in good agreement with the experimental results.

Semiquinone Radical BQH•. In Table 11 are listed the symmetries, vibrational frequencies, and approximate descriptions for the in-plane normal modes of the semiquinone radical obtained by using various methods. The experimental frequencies reported by Tripathi and Schuler[53] are also included in the table for comparison. The isotopic shifts calculated for the deuterated species using BP86/6-31G(d,p) force field are summarized in Table 12 along with the available experimental values.[53] As seen from Table 11, after scaling with 0.89, UHF frequencies are lower than those obtained using other methods. All three parameter HF/DF methods (B3LYP, B3P86, and B3PW91) are found to produce similar results. The SVWN frequencies are also comparable to the HF/DF results. BLYP and BP86 calculations yield frequency values which are intermediate between the UHF and HF/DF frequencies. Tripathi and Schuler[53] assigned the most intense RR band observed at 1613 cm^{-1} to the CC stretching fundamental. The frequency

TABLE 11: Symmetries, Frequencies, and Approximate Descriptions for the In-Plane Normal Modes of *p*-Benzosemiquinone Radical (BQH$^{\bullet}$) as Obtained by Various Methods

	frequency (cm^{-1})								
sym	UHF[a]	SVWN	BLYP	B3LYP	B3P86	B3PW91	BP86	expt[b]	approx description
a′	1503	1646	1578	1636	1653	1648	1592	1613	CC stretch
	1453	1584	1504	1560	1572	1568	1513	1532	COH bend + CO stretch
	1400	1544	1484	1526	1551	1543	1504	1511	CO stretch
	1374	1496	1430	1475	1486	1482	1441	1432	CC stretch
	1282	1459	1406	1456	1470	1466	1414		CC stretch + CH bend
	1265	1354	1329	1364	1372	1369	1332	1323	CC stretch
	1240	1308	1274	1325	1336	1334	1284		CH bend + CC stretch
	1233	1233	1224	1270	1275	1274	1226		CH bend + CC stretch
	1116	1148	1158	1185	1187	1186	1156		COH bend + CH bend
	1079	1116	1138	1165	1162	1163	1131	1162	CH bend
	1035	1060	1070	1105	1105	1105	1067	1039	CH bend
	937	961	955	986	988	986	954	973	CH bend + CC stretch
	768	838	798	827	837	834	806		ring breath
	733	770	751	780	784	783	755		CC stretch
	599	616	611	632	631	630	609	622	ring bend
	442	455	452	466	465	464	450	469	ring bend

[a] UHF values are uniformly scaled by 0.89. [b] Experimental values of Tripathi and Schuler.[53]

TABLE 12: Frequencies, Isotopic Shifts, and Approximate Descriptions for the In-Plane Normal Modes of *p*-Benzosemiquinone Radical (BQH$^{\bullet}$)

freq		isotopic shifts						
$HOC_6H_4O^{\bullet}$		$DOC_6H_4O^{\bullet}$		$HOC_6D_4O^{\bullet}$		$DOC_6D_4O^{\bullet}$		
BP86	expt[a]	BP86	expt[a]	BP86	expt[a]	BP86	expt[a]	approx description
1592	1613	1	0	30	25	32	26	CC stretch
1513	1532	22		21	17	48		COH bend + CO stretch
1504	1511	−3	−4	23	22	22	21	CO stretch
1441	1432	1	7	74	112	80		CC stretch
1332	1323	31		50		88		CC stretch
1131	1162	0	1	312	327	312		CH bend
1067	1039	−8	−13	275		275		CH bend
954	973	−1	−5	103	118	103		CH bend + CC stretch
806		2		27		32		ring breath
609	622	3		20		22		ring bend
450	469	4		6	7	8		ring bend

[a] Experimental frequencies and isotopic shifts from ref 53.

values calculated for this mode using all of the DF and HF/DF methods are in good agreement with this experimental value. The isotopic shifts for this mode obtained using the BP86 method (Table 12) are comparable to the corresponding experimental values.[53] The weak band observed at 1532 cm^{-1} was assigned[53] to the in-plane COH bend coupled with the CO stretching mode. The strong band at 1511 cm^{-1} was assigned[53] to the CO stretching fundamental. The corresponding frequency values calculated by all of the DF and HF/DF methods show good agreement with these experimental values. The excellent agreement between the calculated and observed isotopic shifts for these modes (Table 12) also supports these assignments. The calculated CC stretching frequencies compare well with the experimental[53] frequencies observed at 1432 and 1323 cm^{-1}. The bands observed at 1162 and 973 cm^{-1} were assigned[53] to CH bend modes. The calculated frequencies and isotopic shifts support these assignments. The experimentally observed band at 1039 cm^{-1} was assigned[53] to the ring breath mode. But, as given in Table 11, the calculated frequencies using various methods show that the normal mode which can be correlated to the observed band at 1039 cm^{-1} is the one with the predominant CH bend. Moreover, the calculated frequency values for the ring breath mode are in the 770−840 cm^{-1} region, similar to the ground state and other transients discussed earlier. Thus, we assign the band at 1039 cm^{-1} to the CH bend rather than to the ring breath mode. The calculated frequencies for the ring bend modes are in good agreement with the corresponding experimental[53] values of 622 and 469 cm^{-1}. In general, the vibrational frequencies and isotopic shifts (hence the mode descriptions) obtained using the DF and HF/DF methods are in excellent agreement with the experimental results reported by Tripathi and Schuler.[53]

Overall, for all of the transient species, the calculations show a definite trend in the structural parameters (particularly C═O, C═C, and C−C bond distances) on going from the ground state (S_0) to the triplet state (T_1) and then to the radical anion ($BQ^{\bullet -}$). In spite of this, the calculated as well as experimental C═O, C═C, and C−C stretching Raman active vibrational frequencies do not show a systematic variation on going from one species to another. This is attributed to the fact that these modes show significant coupling of C═O, C═C, and C−C stretching with the C−H in-plane bend.

Summary

The calculations performed on *p*-benzoquinone and its transient species predict very similar results for both 6-31G(d) and 6-31G(d,p) basis sets, which implies that the addition of polarization functions on H atoms does not seem to improve the accuracy of the calculated values significantly. Hence, for larger and similar systems containing H atoms, the 6-31G(d) basis set can be used.

Comparison of the calculated structural parameters for the ground state using various methods shows that the DF method, SVWN, and the three parameter hybrid HF/DF methods B3LYP, B3P86, and B3PW91 give results in excellent agreement with the experiment. RHF calculations are found to underestimate the bond distances (particularly C═C and C═O), whereas the DF methods BLYP and BP86 are found to overestimate the bond distances. All of the methods considered in the present study reproduce the bond angles well. The structural parameters calculated for the transient species (triplet, semiquinone radical, and semiquinone radical anion) show that the method to method variations in the bond distances follow a trend very similar to that seen for the ground state. For the triplet and radical anion (in both cases the symmetry retained as D_{2h}) C═C and C═O bonds are elongated, whereas C−C bonds are shortened in comparison with those of the ground state. These changes in the structural parameters are consistent with the nature of the singly occupied orbitals in the transient species. The calculated bond distances and bond orders for these two species show that the structure of the triplet is intermediate between those of the ground state and radical anion. Semiquinone radical is obtained by the addition of an H atom to one of the oxygens of the triplet. This results in a change of symmetry to C_s. The calculated structural parameters for this species show a mixed aromatic and quinonoid character.

The calculated harmonic vibrational frequencies for the ground state and transient species are assigned by carrying out normal mode analysis. In the structure sensitive region of 1300−1700 cm^{-1}, frequencies obtained for the ground state at the RHF level are overestimated even after scaling with the empirical factor of 0.89, and the mode descriptions are not very accurate. In this region BLYP and BP86 calculations reproduce the experimental frequencies without any scaling. SVWN and HF/DF methods are found to overestimate the frequencies by 2−4%. In general, below 1300 cm^{-1}, these methods show good agreement with the experimental frequencies. Considering the fact that the comparison is made with experimental frequencies from solution phase studies involving anharmonicity, solvent effect, etc., the best agreement is shown by the HF/DF methods. Overall, for the transient species, the BLYP frequencies are comparable to the results of the BP86 method. The SVWN method predicts frequency values intermediate between the other DF methods and HF/DF methods.

The excellent agreement seen between the calculated (using HF/DF methods) and experimental structural parameters as well as vibrational frequencies for the ground state and that seen between the calculated (using HF/DF methods) and experimental frequencies for the transient species clearly indicate that the structures of the transient species obtained using the hybrid HF/DF methods B3LYP, B3P86, and B3PW91 may be considered as equivalent to the experimentally determined structures. However, if we are interested only in the qualitative assignment of the vibrational frequencies of the transient species such as, triplet state, radical anions, or radicals, the best results are obtained by BP86 calculations, particularly in the structure sensitive region. Moreover, the best overall agreement of the calculated isotopic shifts using the BP86 method with the experimental values shows that the calculated normal mode descriptions are accurate.

Acknowledgment. We thank the Jawaharlal Nehru Center for Advanced Scientific Research (JNCASR), the National Laser Programme of the Department of Science and Technology (DST), and the Council of Scientific and Industrial Research (CSIR) for financial support.

Supporting Information Available: Tables of the calculation results using the 6-131G(d) basis set (12 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Hess, B. A., Jr.; Schaad, L. J.; Carsky, P.; Zahradnik, R. *Chem. Rev.* **1986**, *86*, 709.

(2) Paar, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(3) Jones, R. O.; Gunnarsson, O. *Rev. Mod. Phys.* **1989**, *61*, 689.

(4) Labanowski, J. K., Andzelm, J., Eds. *Density-Functional Methods in Chemistry*; Springer-Verlag: New York, 1991.

(5) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.

(6) Andzelm, J.; Wimmer, E. *J. Chem. Phys.* **1992**, *96*, 1280.

(7) Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 5612.

(8) Rauhut, G.; Pulay, P. *J. Phys. Chem.* **1995**, *99*, 3093.

(9) Rauhut, G.; Pulay, P. *J. Am. Chem. Soc.* **1995**, *117*, 4167.

(10) Martin, J. M. L.; El-Yazal, J.; Francois, J. P. *Chem. Phys. Lett.* **1995**, *242*, 571.

(11) Boesch, S. E.; Wheeler, R. A. *J. Phys. Chem.* **1995**, *99*, 8125.

(12) Nonella, M.; Tavan, P. *Chem. Phys.* **1995**, *199*, 19.

(13) Nonella, M.; Brandli, C. *J. Phys. Chem.* **1996**, *100*, 14549.

(14) Nonella, M. *J. Mol. Struct. (THEOCHEM)* **1996**, *362*, 7.

(15) Kozlowski, P. M.; Jarzecki, A. A.; Pulay, P. *J. Phys. Chem.* **1996**, *100*, 7007.

(16) Wong, M. W. *Chem. Phys. Lett.* **1996**, *256*, 391.

(17) El-Azhary, A. A.; Suter, H. U. *J. Phys. Chem.* **1996**, *100*, 15056.

(18) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(19) Morton, R. A., Ed. *Biochemistry of Quinones*; Academic Press: New York, 1965.

(20) Patai, S., Ed. *The Chemistry of Quinonoid Compounds*; Wiley: New York, 1974.

(21) Berger, S.; Hertl, P.; Rieker, A. *Chem. Quinanoid Compd.* **1988**, *2*, 39.

(22) Trotter, J. *Acta Crystallogr.* **1960**, *13*, 86.

(23) Hagen, K.; Hedberg, K. *J. Chem. Phys.* **1973**, *59*, 158.

(24) Chipman, D. M.; Prebenda, M. F. *J. Phys. Chem.* **1986**, *90*, 5557.

(25) Liu, R.; Zhou, X.; Pulay, P. *J. Phys. Chem.* **1992**, *96*, 4255.

(26) Yamakita, Y.; Tasumi, M. *J. Phys. Chem.* **1995**, *99*, 8524.

(27) Zhao, X.; Imahori, H.; Zhan, C. G.; Mizutani, Y.; Sakata, Y.; Kitagawa, T. *Chem. Phys. Lett.*, in press.

(28) Stammreich, H.; Forneris, R. *Z. Naturforsch.* **1952**, *7A*, 756.

(29) Anno, T.; Sado, A. *Bull. Chem. Soc. Jpn.* **1958**, *31*, 734.

(30) Davies, M.; Prichard, F. E. *Trans. Faraday Soc.* **1963**, *59*, 1248.

(31) Becker, E. D.; Charney, E.; Anno, T. *J. Chem. Phys.* **1965**, *42*, 942.

(32) Anno, T. *J. Chem. Phys.* **1965**, *42*, 932.

(33) Palmo, K.; Pietila, L. O.; Mannfors, B.; Karonen, A.; Stenman, F. *J. Mol. Spectrosc.* **1983**, *100*, 368.

(34) Pietila, L. O.; Palmo, K.; Mannfors, B. *J. Mol. Spectrosc.* **1985**, *112*, 104.

(35) Pietila, L. O.; Palmo, K.; Mannfors, B. *J. Mol. Spectrosc.* **1986**, *116*, 1.

(36) Becker, E. D. *J. Phys. Chem.* **1991**, *95*, 2818.

(37) Tripathi, G. N. R. *J. Chem. Phys.* **1981**, *74*, 6044.

(38) Tripathi, G. N. R.; Schuler, R. H. *J. Chem. Phys.* **1982**, *78*, 2139.

(39) Schuler, R. H.; Tripathi, G. N. R.; Prebenda, M. F.; Chipman, D. M. *J. Phys. Chem.* **1983**, *87*, 5357.

(40) Schuler, R. H.; Tripathi, G. N. R.; Prebenda, M. F.; Chipman, D. M. *J. Phys. Chem.* **1983**, *87*, 3101.

(41) Tripathi, G. N. R.; Sun, Q.; Schuler, R. H. *Chem. Phys. Lett.* **1989**, *156*, 51.

(42) Beck, S. M.; Brus, L. E. *J. Am. Chem. Soc.* **1982**, *104*, 1103.

(43) Beck, S. M.; Brus, L. E. *J. Am. Chem. Soc.* **1982**, *104*, 4789.

(44) Rossetti, R.; Beck, S. M.; Brus, L. E. *J. Phys. Chem.* **1983**, *87*, 3058.

(45) Hester, R. E.; Williams, K. P. J. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 573.

(46) Clark, B. R.; Evans, D. H. *J. Electroanal. Chem.* **1976**, *69*, 181.

(47) Bauscher, M.; Mantele, W. *J. Phys. Chem.* **1992**, *96*, 11101.

(48) Neta, P.; Fessenden, R. W. *J. Phys. Chem.* **1974**, *78*, 523.

(49) Prabhananda, B. S. *J. Chem. Phys.* **1983**, *79*, 5752.

(50) Kimura, K.; Yoshinaga, K.; Tsubomura, H. *J. Phys. Chem.* **1967**, *71*, 4485.

(51) Gilando, A.; Zanon, I.; Bozio, R.; Cesare, P. *J. Chem. Phys.* **1978**, *68*, 22.

(52) Wheeler, R. A. *J. Phys. Chem.* **1993**, *97*, 1533.

(53) Tripathi, G. N. R.; Schuler, R. H. *J. Phys. Chem.* **1987**, *91*, 5881.

(54) Pople, J. A.; Schlegel, H. B.; Krishnan, R.; Defrees, D. J.; Binkly, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Chem.* **1981**, *S15*, 269.

(55) Mordzinski, A.; Kownacki, K.; Les, A.; Oyler, N. A.; Adamowicz, L.; Langkilde, F. W.; Wilbrandt, R. *J. Phys. Chem.* **1994**, *98*, 5212.

(56) Armstrong, D. R.; Clarkson, J.; Smith, W. E. *J. Phys. Chem.* **1995**, *99*, 17825.

(57) Ohrstrom, L.; Michaud-Soret, I. *J. Am. Chem. Soc.* **1996**, *118*, 3283.

(58) Jas, G. S.; Wan, C.; Kuczera, K.; Johnson, C. K. *J. Phys. Chem.* **1996**, *100*, 11857.

(59) Keszthelyi, T.; Wilbrandt, R. *J. Mol. Struct.* **1996**, *379*, 211.

(60) Keszthelyi, T.; Wilbrandt, R.; Bally, T. *J. Phys. Chem.* **1996**, *100*, 16843.

(61) Keszthelyi, T.; Wilbrandt, R.; Bally, T.; Roulin, J. L. *J. Phys. Chem.* **1996**, *100*, 16850.

(62) Qin, Y.; Wheeler, R. A. *J. Phys. Chem.* **1996**, *100*, 10554.

(63) Handy, N. C.; Murray, C. W.; Amos, R. D. *J. Phys. Chem.* **1993**, *97*, 4392.

(64) Berces, A.; Ziegler, T. *Chem. Phys. Lett.* **1993**, *203*, 592.

(65) Langhoff, S. R. *J. Phys. Chem.* **1996**, *100*, 2819.

(66) Qin, Y.; Wheeler, R. A. *J. Chem. Phys.* **1995**, *102*, 1689.

(67) Furuya, K.; Torii, H.; Furukawa, Y.; Tasumi, M. *Chem. Lett.* **1996**, 913.

(68) O'Malley, P. J.; Collins, S. J. *Chem. Phys. Lett.* **1996**, *259*, 296.

(69) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864.

(70) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.

(71) Slater, J. C. *Quantum Theory of Molecules and Solids*, Vol. 4: *The Self-Consistent Field for Molecules and Solids*; McGraw-Hill: New York, 1974.

(72) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(73) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(74) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(75) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(76) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

(77) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(78) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(79) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.

(80) Stevens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(81) Perdew, J. P.; Zunger, A. *Phys. Rev. B* **1981**, *23*, 5048.

(82) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gonperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision C.2.; Gaussian Inc.: Pittsburgh, PA, 1995.

(83) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

(84) Sundius, T. MOLVIB. Calculation of Harmonic Force Fields and Vibrational Modes of Molecules, *QCPE* **1991**, *QCMP 103*.

(85) *NMODES* is a package developed in our laboratory which gives normal modes and potential energy distributions in internal coordinates. Since the program generates internal coordinate definitions and other necessary informations automatically, Gaussian output file can be directly used as the input without any modifications. This package can be used to calculate isotopic frequencies and also to facilitate a visual inspection of the normal modes. NMODES can be run on IBM compatible personal computers as well as main frame computers.