1230 *J. Phys. Chem. A* **1998,** *102,* 1230−1235

Effect of Hydrogen Bonding on the Vibrations of *p*-Benzosemiquinone Radical Anion

Chang-Guo Zhan[†] and Daniel M. Chipman*

Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556

Received: October 21, 1997

The vibrational bands experimentally observed for aqueous *p*-benzosemiquinone radical anion are analyzed by use of electronic structure calculations. To clarify the effects of solvation, calculations on the isolated semiquinone anion are compared to those on supermolecule clusters having two to four water molecules strongly hydrogen-bonded at the semiquinone oxygen atoms. The results allow satisfactory assignment of all experimentally known aqueous vibrational bands, some being assigned here for the first time. The clusters considered give reasonable accounts both of the observed frequencies in water and of the frequency shifts between acetonitrile and water that arise from hydrogen bonding.

Introduction

In photosynthesis, light is transformed into chemical energy with a transmembrane proton pump coupled to electron transfer involving the conversion of quinones into hydroquinones.[1−3] Both for the ubiquinones in anoxygenic purple bacteria and the plastoquinones in plant photosystem II, the double reduction process utilizes two quinones which, although often identical, have very different functions. Light energy is utilized to singly reduce Q_A to form the semiquinone radical anion $Q_A^{\bullet-}$, which then reduces Q_B to form the $Q_B^{\bullet-}$ semiquinone and to regenerate Q_A. More light energy is used to again produce $Q_A^{\bullet-}$, which then further reduces $Q_B^{\bullet-}$, which also takes up two protons to ultimately form Q_BH_2. The very different roles of Q_A and Q_B in this process are generally attributed to their different environments in the protein, at least partially due to differential stabilization arising from hydrogen bonding either to water or to nearby amino acid residues.

Resonance Raman and Fourier-transform infrared spectroscopies have been used to investigate the vibrations of quinones and semiquinones in quinoenzymes[4] and in the photosynthetic reaction center.[3,5] However, proper analysis of such experiments is complicated and uncertain. This situation would be alleviated by a more complete understanding of the general effects of hydrogen bonding on the vibrations of semiquinones. As a contribution toward this goal, in this work we utilize electronic structure calculations to interpret and augment the available experimental information on the effect of water on the structure and vibrational properties of the *p*-benzosemiquinone radical anion ($BQ^{\bullet-}$) model system.

There now exists considerable experimental information on the vibrations of $BQ^{\bullet-}$ in different solvents. Detailed resonance Raman spectra have been obtained both in water[6−13] and in acetonitrile.[13] Some limited infrared information is also available in dimethyl sulfoxide,[14,15] acetonitrile,[13,16] and methyl alcohol.[16] Several electronic structure calculations of the force field for isolated $BQ^{\bullet-}$ have also been reported[9,13,17−21] to aid interpretation of the experimental data. However, not all of the bands observed in the most recent and extensive experiments in water[13] have yet been assigned. The present work leads to satisfactory interpretation of all experimentally known aqueous vibrational bands, provides discussion and insights into the general effects of hydrogen bonding in this system, and brings out several points that require further research. In the next section we describe our computational methods, the following section gives results and discussion, and finally a brief summary and conclusion is provided.

Computational Methods

To qualitatively assess the interactions of water molecules with $BQ^{\bullet-}$, a preliminary survey was carried out using empirical molecular mechanics (MM) with the Discover program.[22] The default cvff force field that was originally designed to describe neutral monomers was modified in various ways to be more appropriate for the geometry and charge distribution of the anion solute. In one set of studies, the default model geometry prescribed by the program was retained for every molecule, but an additional charge of −0.5 was added to each of the two solute oxygen atoms to better simulate Coulombic interactions with the semiquinone anion. In other sets of studies, optimized geometries and Mulliken net atomic charges were taken from full electronic structure calculations described below on the isolated solute and solvent monomers. In all cases, monomer geometries were held frozen in the MM studies of intermolecular interactions between $BQ^{\bullet-}$ and one to eight water molecules. Many different starting arrangements were selected in an attempt to locate all possible local minimum conformations of each ensemble. Molecular dynamics with temperatures of 100−300 K was used together with MM energy minimization to equilibrate each ensemble.

Local minimum structures of appropriate semiquinone−water clusters suggested by the MM survey were subjected to refined geometry optimizations of all atoms using density functional theory with the Gaussian 94 program.[23] Becke's 1988 exchange functional[24] with the Perdew−Wang 91 gradient-corrected correlation functional[25] (BPW91) was selected for this purpose on the basis of its superior performance previously found[21] in describing the fundamental vibrations of isolated BQ, $BQ^{\bullet-}$, and BQ^{2-} molecules. Most calculations reported here use the 6-31G** basis set[26,27] augmented with a set of diffuse functions[28] at each oxygen atom of $BQ^{\bullet-}$ and of water, which is denoted[21] as 6-31G**[O+]. As a check, some calculations were also

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[†] Also at Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556.

S1089-5639(97)03400-2 CCC: $15.00

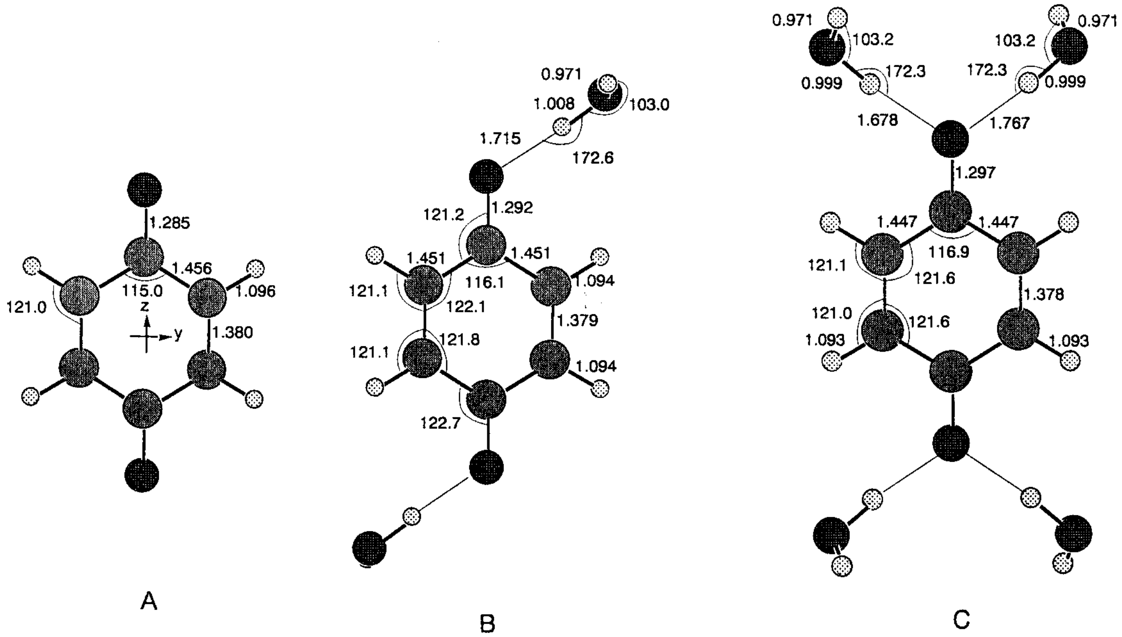

Figure 1. Geometries of (A) $\mathrm{BQ}^{\bullet-}$ (D_{2h}), (B) $\mathrm{BQ}^{\bullet-}$−2w (C_i), and (C) $\mathrm{BQ}^{\bullet-}$−4w (C_i) optimized at the BPW91/6-31G**[O+] level. Bond lengths are given in angstroms and bond angles in degrees.

performed with the 6-31+G** basis[28] that has diffuse functions on all carbon atoms as well as on the oxygens. Vibrational frequencies were obtained from analytic second derivatives evaluated at the computed local minimum geometries. It may be noted that the BPW91/6-31G**[O+] method has been found[21] to reproduce experimental frequencies to within an average absolute deviation of 22 cm^{-1} (or relative absolute deviation of 2.1%) for all 30 fundamental vibrations of the neutral BQ parent molecule and to also provide a good account of the experimentally known vibrations of $\mathrm{BQ}^{\bullet-}$ and BQ^{2-} in acetonitrile.

Results and Discussion

Energies and Optimized Geometries. In the preliminary empirical MM studies, each of the force fields examined led to essentially the same final geometries, with only minor differences in the semiquinone oxygen to water hydrogen distances. These studies indicated that up to four water molecules can simultaneously hydrogen bond with $\mathrm{BQ}^{\bullet-}$, with two different water molecules each forming a single hydrogen bond to one of the $\mathrm{BQ}^{\bullet-}$ oxygen atoms. In actuality, of course, hydrogen bonds are constantly breaking and reforming, so the dynamical average should be less than the maximum number of four hydrogen bonds. This is in qualitative agreement with the results of a more extensive classical molecular dynamics study[29] involving many water molecules using the free energy perturbation method, in which it was found that with a temperature of about 300 K and a pressure of 1 atm each $\mathrm{BQ}^{\bullet-}$ solute molecule makes single hydrogen bonds with about 3.3 water molecules, on the average.

Isolated $\mathrm{BQ}^{\bullet-}$ has high symmetry corresponding to the D_{2h} point group, as indicated in Figure 1. Among the possible $\mathrm{BQ}^{\bullet-}$ −2w structures suggested by the MM studies involving two hydrogen bonds, a typical one having C_i symmetry was selected for detailed investigation, having one water molecule bonded to each semiquinone oxygen atom as shown in Figure 1. The MM studies suggested two possible $\mathrm{BQ}^{\bullet-}$ −4w conformations corresponding to either C_i or D_2 point group symmetry. These differ mainly in the relative twist directions of the dangling water hydrogens at opposite ends of the cluster. The geometry of the C_i form is shown in Figure 1. The D_2 form is very similar, with semiquinone geometrical parameters differing by less than 0.001 Å and 0.1° in all cases. Also, the four equivalent hydrogen bonds in the D_2 form are essentially the average of the two distinct ones in the C_i form, and the four equivalent water molecules have essentially the same internal geometries as those in the C_i form. Furthermore, the D_2 form has semiquinone vibrational frequencies differing from those of the C_i form by 2 cm^{-1} or less in all cases except for one apparently anomalous but actually well-understood mode (see below for discussion of this). Thus, for the most part we present detailed results only for the C_i form as a typical representative of $\mathrm{BQ}^{\bullet-}$−4w. Finally, a nonsymmetric $\mathrm{BQ}^{\bullet-}$−3w structure was also considered, with hydrogen bonds approximately arranged as in the D_2 structure discussed above. Results for the $\mathrm{BQ}^{\bullet-}$−3w cluster are generally found to lie between those found for the $\mathrm{BQ}^{\bullet-}$−2w and $\mathrm{BQ}^{\bullet-}$−4w clusters and so need not be presented in as much detail.

Each of these various supermolecule clusters have nearly planar semiquinone structures, with all hydrogen bonds also lying approximately in the plane of the semiquinone, while the remaining dangling hydrogen atoms of the water molecules are twisted somewhat out of the plane by about 100−140°. Subsequent geometry optimization and vibrational analysis with the BPW91/6-31G**[O+] method verified each of these candidates to be a local minimum structure. More extensive BPW91/6-31+G** calculations on $\mathrm{BQ}^{\bullet-}$−4w led to very minor changes in the geometry and changes of 16 cm^{-1} or less in all vibrational frequencies, mostly toward lower frequencies.

Previous electronic structure calculations on $\mathrm{BQ}^{\bullet-}$−4w have been carried out with overall D_{2h} symmetry,[30,31] and calculations on $\mathrm{BQ}^{\bullet-}$−2w have been carried out with overall C_{2h} symmetry.[31] The present results suggest that such high-symmetry configurations[30,31] which constrain all atoms to lie in one plane are probably saddle points connecting lower symmetry local minimum structures related by twisting of the water molecules about the hydrogen bond axes. Such rotation of the hydrogen bonds was noted in our molecular dynamics simulation to be common even at the very low temperature of 100 K, indicating that the energy barrier for rotating the hydrogen bonds between local minima is probably very small. The total energies calculated with the BPW91/6-31G**[O+] method for the local minimum $BQ^{\bullet-}-4w$ structures of C_i and D_2 symmetry differ from one another by only 0.022 kcal/mol, or 0.035 kcal/mol after including zero-point vibrational energy corrections. Thus, these structures will have essentially equal probabilities and may well interconvert frequently.

The BPW91/6-31G**[O+] total energies for the supermolecule clusters compared to the energies of the isolated monomers indicate an average hydrogen bond energy per water molecule of 12.8 kcal/mol in $BQ^{\bullet-}-2w$, 12.2 kcal/mol in $BQ^{\bullet-}-3w$, and 11.7 kcal/mol in $BQ^{\bullet-}-4w$. We do not claim that these are quantitatively representative of physical dissociation energies in aqueous solution, due to expected significant corrections from basis set superposition errors, from zero-point energy differences, and from the influence of bulk water molecules that are not included here. However, we do put these results forward as strong evidence that the presence of one strongly hydrogen-bonded water molecule at each semiquinone oxygen atom does not significantly diminish its capacity to form another hydrogen bond of almost equal strength to another water molecule.

The BPW91/6-31G**[O+] optimized geometry for isolated $BQ^{\bullet-}$ shown in Figure 1 is very similar to those reported earlier[13,17−20,32,33] as obtained by various other methods of electronic structure calculation. This geometry is quite adequately discussed in several of those references, so we focus here only on the small but significant changes in semiquinone geometry caused by hydrogen bonding. These changes are found to be roughly additive in the number of strongly hydrogen-bonded water molecules, so it is sufficient to discuss changes just with the representative $BQ^{\bullet-}-4w$ cluster.

The most significant semiquinone geometry changes in $BQ^{\bullet-}-4w$ compared to isolated $BQ^{\bullet-}$ are a lengthening of the two CO bonds by 0.012 Å, a shortening of the four nominal CC single bonds by 0.009 Å, and an increase of the two apex CCC bond angles by 2°. Note particularly that the two nominal CC double bonds change very little. On the basis of these observations, we may expect that in the hydrogen-bonded clusters the weakened CO bonds will have lower stretching frequencies and the stronger CC single bonds will have higher stretching frequencies than in isolated $BQ^{\bullet-}$.

The calculations indicate that the O···HO bonds are within 7−8° of being linear in all cases, and the calculated O···H hydrogen bond distances all lie in the reasonably narrow range of 1.678−1.767 Å. Interestingly, the extremes of this latter range are found for neighboring water molecules in the same cluster.

The water molecules themselves have very nearly the same geometry in all the calculated clusters. The OH bond length is shortened by about 0.001 Å from its calculated free-molecule value of 0.972 Å, while the HOH bond angle is reduced by about 2° from its calculated free-molecule value of 105.0°. In the gas phase, distortion of a single water molecule from its calculated equilibrium geometry to its geometry in a typical hydrogen-bonded cluster with semiquinone anion would require about 0.7 kcal/mol. Because of the absence of additional water molecules to simulate bulk solvent in the present calculations, these observations should be regarded only as suggestive of the qualitative conclusion that the hydrogen-bonded water molecules have small but significant distortions from their free-molecule geometries.

Calculated Vibrational Frequencies. The harmonic vibrational frequencies of $BQ^{\bullet-}$ with D_{2h} symmetry, $BQ^{\bullet-}-2w$ with C_i symmetry, and $BQ^{\bullet-}-4w$ with C_i symmetry all calculated at the BPW91/6-31G**[O+] level are listed in Table 1. Strictly speaking, vibrational modes of the lower symmetry hydrogen-bonded clusters do not form basis vectors for the D_{2h} point group of the isolated semiquinone anion. However, in all cases the perturbations due to hydrogen bonding were small enough that each vibration in the lower symmetry clusters could be unambiguously associated with one in the isolated parent $BQ^{\bullet-}$. Therefore, for clarity it is convenient to discuss all modes in terms of labeling based on a quasi-D_{2h} symmetry.

In addition to the results listed for the 30 internal semiquinone vibrations, the supermolecule clusters also have additional modes associated with the water molecules. For the most part, these are of little interest because such a small number of water molecules cannot provide a reasonable representation of the corresponding modes that would be found with bulk solvent. All the pseudotranslational modes of the water molecules, along with some of their librational modes, are calculated to be lower than 206 cm^{-1}, the HOH bends range from 1646 to 1656 cm^{-1}, and the OH stretches lie above 3100 cm^{-1}, which therefore mix only slightly with semiquinone vibrations. The remaining librational water modes are usually calculated near 420−445 cm^{-1} or 800−900 cm^{-1}, and in a few cases one of these happens to be accidentally nearly degenerate with an internal semiquinone vibration leading to strong mixing to produce split modes of approximately equal semiquinone and water character. Thus, one particular combination of the water librational motions mixes somewhat with the lowest frequency b_{2u} semiquinone motion to produce split modes at 411 and 450 cm^{-1} in $BQ^{\bullet-}-2w$, and even stronger mixing leads to split modes at 401 and 457 cm^{-1} in $BQ^{\bullet-}-4w$. Similarly, one particular combination of the water librational motions mixes with the second lowest frequency a_g semiquinone motion to produce split modes at 808 and 839 cm^{-1} in $BQ^{\bullet-}-4w$. In Table 1 we report only the lower frequency from each of these pairs. Inclusion of additional outer-shell water molecules in the calculation would presumably alter these water librational motions, so the frequencies for the noted accidental mixings should be regarded as artifacts of the present calculations.

Changes in internal semiquinone anion vibrational frequencies due to hydrogen bonding are calculated to be modest, always less than 50 cm^{-1}. In nearly all cases, the calculated frequency shifts change monotonically from $BQ^{\bullet-}$ to $BQ^{\bullet-}-2w$ to $BQ^{\bullet-}-4w$. The only exceptions are the second lowest a_g and the lowest b_{2u} modes, which show an increase in frequency on going from $BQ^{\bullet-}$ to $BQ^{\bullet-}-2w$ but then decrease slightly from $BQ^{\bullet-}-2w$ to $BQ^{\bullet-}-4w$. These apparent anomalies in $BQ^{\bullet-}-4w$ are simply due to the accidental mixings with water librational modes that were discussed just above.

In nearly all cases the shifts caused by hydrogen bonding are to higher frequencies. The only exceptions are shifts to lower frequencies in the two CO stretches, as expected due to the weakened CO bonds discussed above, and a very slight drop in the second b_{2g} mode. In general, just as with geometry changes it can be concluded that frequency shifts due to hydration are approximately additive in the number of hydrogen-bonded water molecules.

Assignments of the Experimental Spectra. Also listed in Table 1 for comparison are experimental frequencies measured in acetonitrile and in water. To the extent that dynamic solvation effects may provide temporary structures of low symmetry or of no symmetry at all, it should be noted that the selection rules

TABLE 1: Calculated BPW91/6-31G[O+] and Experimental Fundamental Vibrational Frequencies and Isotopic Shifts for *p*-Benzosemiquinone Radical Anion. All Frequencies Are in cm^{-1}**

	calculated						experimental		
mode	BQ$^{\bullet-}$ [a]	BQ$^{\bullet-}$−2w	BQ$^{\bullet-}$−4w	d_4[b]	$^{13}C_6$[b]	$^{18}O_2$[b]	BQ$^{\bullet-}$ [c]	BQ$^{\bullet-}$ (aq)[d]	d_4[b,e]
a_g	454	464	480	−5	−8	−14	470	484	−1
a_g	806	814	808	−25	−21	−3	819	830	−33
a_g	1128	1138	1150	−325	−3	−1	1143	1162	−317
a_g	1448	1440	1434	−6	−37	−25	1452	1434	−9
a_g	1609	1616	1621	−30	−57	−1	1609	1620	−23
a_g	3100	3126	3135	−811	−10	0			
b_{3g}	453	475	487	−22	−10	−8	497		
b_{3g}	612	618	621	−22	−18	−6	638		
b_{3g}	1229	1244	1256	−254	−19	−1	1257	1271	−251
b_{3g}	1416	1430	1440	−39	−46	0	1453	1471	−79
b_{3g}	3073	3101	3116	−819	−10	0			
b_{1u}	768	775	778	−76	−14	−17	780		
b_{1u}	943	951	957	−102	−27	0			
b_{1u}	1329	1330	1331	−155	−21	−13	1347		
b_{1u}	1502	1500	1500	−32	−39	−10			
b_{1u}	3074	3101	3115	−820	−9	0			
b_{2u}	377	411	401	−2	−1	−10			
b_{2u}	1051	1068	1082	−291	−14	0	1046	1060	
b_{2u}	1224	1248	1265	−40	−39	−1			
b_{2u}	1477	1484	1489	−40	−51	−1	1506	1512	
b_{2u}	3094	3119	3132	−811	−10	0			
a_u	375	378	379	−42	−12	0			
a_u	907	921	929	−191	−8	0			
b_{3u}	127	130	132	−2	−1	−4			
b_{3u}	503	508	511	−90	−10	−1	525		
b_{3u}	833	839	844	−88	−15	−1			
b_{1g}	744	753	755	−166	−6	0	748	762	
b_{2g}	304	308	308	−14	−8	−3			
b_{2g}	730	729	728	−80	−26	−2			
b_{2g}	918	929	936	−151	−7	0			

[a] Results from previously reported calculation.[21] [b] d_4, $^{13}C_6$, and $^{18}O_2$ columns give the frequency shift in BQ$^{\bullet-}$−4w due to the indicated isotopic substitution. [c] Bands observed in acetonitrile[13] and assigned in a previous calculation.[21] [d] Bands observed in water.[13] [e] Bands observed in water.[11,12]

for vibrational intensities that are normally expected for highly symmetrical structures may break down to allow weak intensities for nominally forbidden bands.

The most recent experimental resonance Raman studies of BQ$^{\bullet-}$ in water[13] report 13 vibrational modes at 484, 762, 830, 964, 1060, 1162, 1271, 1311, 1434, 1471, 1512 or 1513, 1620, and 1667 cm^{-1}. Ten of these have been observed and satisfactorily assigned in earlier resonance Raman studies.[6−12] Thus, the bands at 484, 830, 1162, 1434, and 1620 cm^{-1} are totally symmetric a_g fundamental modes, the bands at 964, 1311, and 1667 cm^{-1} are the overtone and combination bands of the 484 and 830 cm^{-1} fundamentals, and the 1271 and 1471 cm^{-1} bands are fundamentals of b_{3g} symmetry that gain intensity through vibronic coupling.

The calculations presented in this work will be used to aid assignment of the remaining very weak bands observed in water[13] at 762, 1060, and 1512 or 1513 cm^{-1}. The more extensive and well-understood data from acetonitrile[13] will also prove very useful for this purpose. Both acetonitrile and water are high dielectric constant solvents. Therefore, the long-range electrostatic effects of solvation on BQ$^{\bullet-}$ should be roughly the same in both solvents, and the shifts between the two solvents may be primarily attributed to the specific interactions due to strong hydrogen bonding in water. These specific interactions are modeled by the hydrogen-bonded clusters in the present calculations. Thus, to the extent that generic dielectric effects may approximately cancel out in the comparison, the shifts calculated between isolated BQ$^{\bullet-}$ and its hydrogen-bonded clusters may provide a reasonable description of the experimental acetonitrile-to-water shifts.

This hypothesis can be readily tested by examining the seven well-understood fundamental bands noted above. Experimental acetonitrile to water shifts are found to be 14, 11, 19, −18, 11, 14, and 18 cm^{-1} for the five a_g and two b_{3g} assigned modes, respectively. The corresponding calculated BQ$^{\bullet-}$ to BQ$^{\bullet-}$−2w shifts are 10, 8, 10, −8, 7, 15, and 14 cm^{-1}, the BQ$^{\bullet-}$−3w shifts are 22, 9, 16, −12, 9, 19, and 19 cm^{-1}, and the BQ$^{\bullet-}$−4w shifts are 26, 2, 22, −14, 12, 27, and 24 cm^{-1}. Thus, the calculated −2w shifts underestimate the experimental ones with an average absolute error of 5 cm^{-1}, the calculated −3w shifts are sometimes smaller and sometimes larger than experiment and give an average absolute error of 4 cm^{-1}, and the calculated −4w shifts generally overestimate the experimental ones with an average absolute error of 7 cm^{-1}. It can be concluded the −2w, −3w, and −4w theoretical models all provide a qualitatively correct picture of the experimental shifts, except for the second a_g mode in the BQ$^{\bullet-}$−4w cluster, which has accidental anomalous behavior due to reasons discussed above.

Three fundamental vibrations calculated at 768 (b_{1u}), 744 (b_{1g}), and 730 (b_{2g}) cm^{-1} in isolated BQ$^{\bullet-}$ are close enough in frequency to be considered as reasonable candidates for the experimentally observed band at 762 cm^{-1}. Previous work[13] has indicated that the b_{1u} candidate corresponds to the 780 cm^{-1} band observed by both resonance Raman and infrared spectroscopy in acetonitrile. Assignment to that mode would imply a negative experimental shift of −18 cm^{-1} between acetonitrile and water, which is very unlikely in light of the positive calculated shifts of 7 and 10 cm^{-1} between isolated BQ$^{\bullet-}$ and its −2w and −4w clusters, respectively. Previous work[13] has indicated that the b_{1g} candidate corresponds to the 748 cm^{-1} band observed in acetonitrile. This would imply a positive experimental shift of 14 cm^{-1} between acetonitrile and water, which is in reasonable agreement with the calculated shifts just noted. The remaining possibility of assignment to the b_{2g}

candidate is less likely due to the larger frequency discrepancy between calculation and experiment and to the fact that this mode has not been observed in acetonitrile either. We therefore propose the b_{1g} mode as the most likely assignment for the observed 762 cm^{-1} band.

The b_{2u} fundamental vibration calculated at 1051 cm^{-1} in isolated $BQ^{\bullet -}$ is the only candidate close enough in frequency to be reasonably considered for the experimentally observed band at 1060 cm^{-1}. Previous work[13] has indicated that this candidate corresponds to the 1046 cm^{-1} band observed in acetonitrile. This would imply an experimental shift of 15 cm^{-1} between acetonitrile and water, which is in reasonable agreement with the calculated shift of 17 and 32 cm^{-1} between isolated $BQ^{\bullet -}$ and its −2w and −4w clusters, respectively. We may therefore confidently assign this b_{2u} mode to the observed 1060 cm^{-1} band.

The very weak band observed in water by resonance Raman spectroscopy[13] at 1512 or 1513 cm^{-1} almost certainly corresponds to the very strong infrared band reported in that same work to be at 1506 cm^{-1} in acetonitrile. Another infrared study[16] reported it at 1508 cm^{-1} in methyl alcohol and at 1504 cm^{-1} in acetonitrile, which confirms the positive direction of the shift due to hydrogen bonding. In earlier infrared studies[14−16] this band was attributed to the asymmetric CO stretch motion, which has b_{1u} symmetry. However, in the most recent and extensive experimental study[13] this band was assigned to the asymmetric CC stretch motion involving the nominally doubly bonded interior ring carbon atoms, which has b_{2u} symmetry, on the basis of the small $^{16}O_2$-to-$^{18}O_2$ isotope shift of only −3 cm^{-1} observed in acetonitrile. Previous theoretical calculations[21] on isolated $BQ^{\bullet -}$ provided additional support for the latter assignment based on the oxygen isotope shift data.

The 1512 or 1513 cm^{-1} observed band is closer in frequency to the candidate CO stretch at 1502 cm^{-1} than to the candidate CC stretch at 1477 cm^{-1} calculated in isolated $BQ^{\bullet -}$. But a more powerful argument is obtained from the observed[13] acetonitrile-to-water positive shift of 6−7 cm^{-1}, which qualitatively disagrees with the *negative* shifts in frequency of −2 cm^{-1} calculated for the CO mode between isolated $BQ^{\bullet -}$ and each of its −2w, −3w, and −4w clusters. However, it agrees well with the calculated positive shifts of 7, 9, and 12 cm^{-1} for the CC mode in the −2w, −3w, and −4w clusters, respectively. This is strong additional evidence that the intense infrared band corresponds to CC rather than CO motions. Unfortunately, the problem is not completely settled because, just as noted previously[20] for isolated $BQ^{\bullet -}$, the present calculations on clusters indicate high infrared intensity for the CO motions, but very low infrared intensity for CC motions, which would instead favor the earlier assignments[14−16] to CO motions. We believe that the small oxygen isotope shift and positive hydrogen bond shift arguments are more convincing than the inverted IR intensity consideration, which may suffer from an inadequate level of theory, and so provisionally support the assignment of this mode to CC motions. However, further theoretical and experimental work should still be carried out to definitively settle this matter.

For completeness, and as an aid to further experimental work, we also give in Table 1 the calculated isotope shifts for d_4, $^{13}C_6$, and $^{18}O_2$ substitution in the $BQ^{\bullet -}$−4w cluster. These turn out to all be very close to those isotope shifts reported previously[21] for the analogous calculations on isolated $BQ^{\bullet -}$. The calculated d_4 isotope shifts are compared in Table 1 with the seven shifts known experimentally in water. Six of the experimental d_4 isotope shifts in water are reproduced within 8 cm^{-1} by the calculations. The only exception is a large error for the fourth b_{3g} mode, which is calculated to be −39 cm^{-1} but observed to be −79 cm^{-1}. However, it should be noted that the d_4 isotope shift for this mode measured in acetonitrile[13] is −41 cm^{-1}, which agrees very well with the present and previous[21] calculations. It is extremely difficult to imagine a process that could produce such a large experimental acetonitrile-to-water solvation effect on a d_4 isotope shift, and we therefore recommend an experimental reinvestigation of this mode for the perdeuterated form in water.

Evaluation of Cluster Models. Nearly all the calculated vibrational frequencies for $BQ^{\bullet -}$−3w are found to lie between the corresponding frequencies calculated for the −2w and −4w clusters. The only exceptions are for the second a_g mode calculated at 815 cm^{-1}, which is slightly above the −2w cluster but also higher than the −4w clusters because of the anomalous behavior of the latter for this mode that has been discussed above, and a very minor discrepancy in the lowest b_{2g} mode lying at 307 cm^{-1} in the −3w cluster as compared to 308 cm^{-1} in both the −2w and −4w clusters.

Considering all 10 of the assigned fundamental modes, we find average absolute deviations of 19, 15, and 14 cm^{-1} from the experimental results in water for the calculated −2w, −3w, and −4w clusters, respectively. These are comparable to the average absolute deviation of 16 cm^{-1} for isolated $BQ^{\bullet -}$ from the experimental results in acetonitrile and improve considerably on the deviation of 30 cm^{-1} for isolated $BQ^{\bullet -}$ from the experimental results in water. Most calculated frequencies lie below the experimental ones. The apparently better performance of the larger clusters in this comparison may therefore simply be due to a systematic underestimation of force constants in the theoretical calculations partially canceling with the mostly positive frequency shifts arising from hydrogen bonding, thereby artificially reducing the errors. Thus, we conclude from these observations only that each of the clusters considered gives a qualitatively correct account of the observed frequencies in water.

Considering frequency shifts due to hydrogen bonding, we obtain average absolute deviations of 5, 5, and 7 cm^{-1} from the 10 assigned experimental acetonitrile-to-water shifts for the calculated −2w, −3w, and −4w clusters, respectively. The −2w and −3w clusters give some shifts to be smaller and some larger than experiment, while the −4w cluster generally gives most shifts larger than experiment. However, the overall deviations are close enough that we simply conclude that each of the cluster models also gives a satisfactory account of the observed shifts due to hydrogen bonding.

Conclusion

The results of this work provide a reasonable description of all the observed vibrational bands of *p*-benzosemiquinone radical anion in water, some being assigned here for the first time. It is found that $BQ^{\bullet -}$ can form hydrogen bonds of approximately equal strength with each of up to four water molecules. Cluster models having two, three, and four strong hydrogen bonds to water all provide a satisfactory description of the experimental frequencies in water and also of the acetonitrile-to-water frequency shifts that arise from hydrogen bonding.

The lower symmetry associated with the three-water model, and the lack of any symmetry in the myriad of other possible structures that would arise from dynamic solvation effects, could provide an explanation for experimental observation of nominally forbidden ungerade vibrational modes in the resonance Raman spectrum. Indeed, our assignments indicate that two of the very weak observed bands correspond to modes of b_{2u} symmetry. The one of those near 1500 cm^{-1} almost certainly corresponds to the intense band observed in several solvents with infrared spectroscopy. Strong evidence from both oxygen isotope and hydrogen-bonding shifts indicates that this band should be assigned to asymmetric CC motions, although weaker evidence from calculated intensities support instead the earlier assignment to asymmetric CO motions. Further experimental and theoretical work is recommended to definitively settle this matter.

In summary, this study has contributed to a more complete understanding of the vibrational modes of *p*-benzosemiquinone radical anion in water. The strong hydrogen bonding with water molecules raises most vibrational frequencies, with the notable exception that the CO bonds become weakened and have lower stretching frequencies in water than in acetonitrile.

Acknowledgment. The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Contribution No. NDRL-4037 from the Notre Dame Radiation Laboratory.

References and Notes

(1) *The Chemistry of Quinonoid Compounds*; Patai, S., Ed.; John Wiley & Sons: New York, 1974.

(2) *Functions of Quinones in Energy Converting Systems*; Trumpower, B. L., Ed.; Academic: New York, 1982.

(3) Okamura, M. Y.; Feher, G. *Annu. Rev. Biochem.* **1992**, *61*, 881, and references therein.

(4) Klinman, J. P.; Mu, D. *Annu. Rev. Biochem.* **1994** *63*, 299, and references therein.

(5) Breton, J.; Boullais, C.; Berger, G.; Mioskowski, C.; Nabedryk, E. *Biochemistry* **1995**, *34*, 11606, and references therein.

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

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

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

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

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

(11) Tripathi, G. N. R. In *Advances in Spectroscopy*; Clark, R. J. H., Hester, R. E., Eds.; Wiley: New York, 1989; Vol. 18, pp 157−218.

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

(13) Zhao, X.; Imahori, H.; Zhan, C.-G.; Sakata, Y.; Iwata, S.; Kitagawa, T. *J. Phys. Chem. A* **1997**, *101*, 622.

(14) Tallant, D. R.; Evans, D. H. *Anal. Chem.* **1969**, *41*, 835.

(15) Clark, B. R.; Evans, D. H. *J. Electroanal. Chem. Interfacial Electrochem.* **1976**, *69*, 81.

(16) Bauscher, M.; Mäntele, W. *J. Phys. Chem.* **1992**, *96*, 11101.

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

(18) Raymond, K. S.; Wheeler, R. A. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 665.

(19) Nonella, M. *J. Phys. Chem. B* **1997**, *101*, 1235.

(20) Mohandas, P.; Umapathy, S. *J. Phys. Chem. A* **1997**, *101*, 4449.

(21) Zhan, C.-G.; Iwata, S. *Chem. Phys.*, in press.

(22) *Discover;* Biosym/MSI; San Diego, 1995.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, 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.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision D.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

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

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

(26) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(27) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(28) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

(29) Raymond, K. S.; Grafton, A. K.; Wheeler, R. A. *J. Phys. Chem. B* **1997**, *101*, 623.

(30) O'Malley, P. J. *J. Phys. Chem. A* **1997**, *101*, 6334.

(31) O'Malley, P. J. *Chem. Phys. Lett.* **1997**, *274*, 251.

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

(33) Liu, R.; Zhou, X. *J. Phys. Chem.* **1993**, *97*, 9613.