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The other phenomenon which occurs in this temperature range is a transition to a poorly hydrated, rigidly packed gel phase.[1-6] This transition occurs over several days when the sample is incubated near 0 °C.[1] We believe the transition reported herein is a separate event for three reasons. Firstly, the time scale of our experiments only encompasses part of the first, rapid stage[5,6] of the incubation. Secondly, the rate of change on incubation decreases as the chain length increases;[1] we have incubated a DBPC gel at 3 °C for 10 days and found no evidence of any change in the system. Finally, incubation of DPPC results in decreased mobility of the acyl chains,[2-6] an effect opposite to that observed in the transition reported in this study.

Apart from the details of the structural changes resulting from the transition, there are a variety of other points to be addressed. It will be of interest to learn if the transition is a general property of phospholipids or, indeed, surfactants. The behavior of the choline band suggests that there may be subtle differences in, at least, the head group region between samples hydrated with H_2O and D_2O. There is also the point as to what occurs when the amount of water is exactly, or less than, that required to fully hydrate the lipid, these studies having been performed in the presence of excess water. We are currently addressing these questions and expect to report on them in the near future.

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Registry No. DPPC, 63-89-8; DBPC, 37070-48-7; water, 7732-18-5.

Resonance Raman and Molecular Orbital Studies of the Effects of Deuteration on the Vibrational Structure of the *p*-Benzosemiquinone Radical Anion[1]

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Deuterium substitution of the *p*-benzosemiquinone radical anion results in decreases of 23 and 317 cm^{-1} in the vibrational frequencies of its totally symmetric ring stretching (Wilson 8a) and C–H bending (9a) modes as observed by resonance-enhanced Raman methods. Ab initio molecular orbital calculations corroborate the vibrational assignments and predict decreases of a similar magnitude. Both the experimental and theoretical studies show that the bands associated with the CO stretching and C–C–C bending vibrations are affected to only a very minor extent by deuteration, i.e., that there is very little contribution from local modes involving hydrogen motion. The symmetrical ring breathing (1) and C–H stretching (2) modes are not resonance enhanced and not observed in the Raman experiments. Of particular note is the Raman band at the ring stretching frequency of the deuterated radical which is considerably broader than the other lines in H_2O and partially resolved into two lines in D_2O. This feature is tentatively interpreted as being due to an accidental near degeneracy with the combination of the 9a and 1 modes. Deuteration of the radical somewhat simplifies its optical absorption spectrum in the region of 400–410 nm indicating that the frequency of the 9a vibration in the excited state is decreased in much the same way as in ground state.

Radicals related to the *p*-benzosemiquinone anion are important in electron transport processes so that it is of considerable interest to obtain detailed information on their electronic and molecular properties. The unsubstituted *p*-benzosemiquinone radical anion is relatively stable and can be readily prepared in aqueous solution under well-controlled conditions by radiation chemical oxidation of hydroquinone. The frequencies of the totally symmetric vibrations of this radical have been previously determined by resonance Raman methods[3,4] and assignments made from symmetry and structural considerations. Recent[5] ab initio molecular orbital studies of the vibrational structure of this radical provide information on the 30 possible vibrational modes and completely confirm the assignments made in the Raman experiments. Of interest, particularly with respect to the comparisons between theory and experiment, are the effects of deuterium substitution on the vibrational frequencies since the isotope effects provide information on the contributions from local modes involving hydrogen motion. We report here the results of experimental and theoretical studies in which effects of deuteration on the Raman spectra of this important radical are examined. Also reported are the effects of deuterium substitution on the absorption and ESR spectra of this radical.

Experimental Section

The Raman studies were carried out by OH oxidation of 2 mM hydroquinone directly in the Raman cell (0.2 cm^3) by pulse radiolytic methods.[4] Spectra were examined at microsecond times after production of radical concentrations of $\sim 10^{-4}$ M. This approach allows one to avoid complications from product buildup which are present when chemical oxidation methods are used. Data were recorded at the rate of 7.5 experiments/s. Studies were at pH $\sim$11 where the radical does not decay on the time scale of these experiments. Flow rates of $\sim 2\ cm^3/s$ were used to replenish the sample between pulses.

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TABLE I: Raman Frequencies of *p*-Benzosemiquinone Totally Symmetric Fundamental Vibrations in H_2O

		ν_H		ν_D		$\nu_H - \nu_D$	
mode	Wilson designation	calcd × 0.89	exptl[a]	calcd × 0.89	exptl[a]	calcd × 0.89	exptl[a]
C-C-C bend	6a	463	481 (13)	459	480 (13)	−3	−1
ring breath	1	781	[b] (<1)	755	[b] (<1)	−26	[b]
C-H bend	9a	1147	1161 (24)	829	844 (10)	−318	−317
C-O stretch	7a	1388	1435 (23)	1382	1426 (23)	−6	−9
C-C stretch	8a	1607	1620[c] (100)	1574	1597[d] (100)	−33	−23
C-H stretch	2	2983	[b] (<1)	2212	[b] (<1)	−771	[b]

[a] Intensitives are given parenthetically relative to amplitude of 8a vibration = 100. [b] Not observed. [c] In D_2O this frequency is increased to 1621.5 cm^{-1}. [d] Band is complicated by overlap with nonresonance-enhanced vibration (see text). Experiments in D_2O place limits of 1592–1603 cm^{-1} on this frequency (see Figure 4).

The Raman signal was excited with a $\sim$10-ns pulse from a Lambda Physik 2001 dye laser pumped at 308 nm and detected with an optical multichannel analyzer using an intensified silicon photodiode array (PAR 1420-3) as described elsewhere.[6] A spex 1402 polychromator was used for dispersion ($\sim$25 cm^{-1}/mm) of the scattered radiation. With a slit width of 0.2 mm the band width of the detection system was $\sim$5 cm^{-1}. Absolute Raman frequencies were measured by comparison with observations on acetonitrile, benzene, carbon tetrachloride, and ethanol. In general, line positions of the stronger lines are known to $\sim$1 cm^{-1}. Differences between the Raman frequencies of the protonated and deuterated radical were made by direct comparison and depend only on the dispersion of the polychromator so that these differences are somewhat more accurate. With excitation at 430 nm the Raman signals are quite intense and a signal-to-noise ratio in the 1600-cm^{-1} band of better than 100/1 was achieved with recording periods of 5 min (2400 pulses). The background was measured in the absence of irradiation and subtracted.

Absorption spectra were recorded both by conventional spectrophotometry (Cary 219 with a computerized data collection system) and by pulse radiolysis methods.[7] In the former case, air oxidation was used to produce the radical. Since the samples deteriorated very rapidly these recordings provide only qualitative information on the changes introduced by deuteration. Oxidation by pulse radiolysis methods was quantitative providing that the solution was carefully prepared so that semiquinone was not initially present in any significant concentration. In this latter case, extinction coefficients could be determined to a few percent by comparison with the thiocyanate dosimeter.[8] ESR spectra were recorded by in situ radiolysis methods.[9]

Hydroquinone was from Eastman Kodak and hydroquinone-d_6 (98% d) from Merck Sharpe and Dohme. ESR experiments indicated that 6% of the radical produced from the latter had one proton on the ring, i.e., confirming that deuteration was 98.5% and that there was no exchange of the ring protons of the substrate with water. No doubly, triply, or quadruply protonated radical was detected in the ESR experiments. Solutions were prepared by thoroughly purging water from a millipore system with N_2O, adding KOH, and finally the hydroquinone. When prepared in this way, the solutions were very near to colorless (the spectrophotometric studies showed the semiquinone concentration to be $<5 \times 10^{-6}$ M) but very sensitive to any admission of oxygen. A number of experiments were also carried out in deuterated water with a 99.9% deuterium content. Raman and ESR experiments were at hydroquinone concentrations of $\sim$2 mM and optical absorption studies at $\sim$0.2 mM.

Ab initio calculations were carried out on a VAX 11/780 computer using the GAMESS program package.[10] The unrestricted Hartree–Fock model was used with the 3-21G basis set[11] throughout. The equilibrium geometry for benzosemiquinone radical anion was obtained by a direct analytic gradient method. The harmonic force const. matrix was calculated by finite displacements of each atom by ±0.01 Å in each Cartesian direction from its calculated equilibrium position. Normal modes were then obtained by diagonalization of the mass-weighted Cartesian force constant matrix and removal of the six modes corresponding to overall translation and rotation. The numerical precision associated with this finite displacement calculation of the force constant matrix is about 10–20 cm^{-1} for the final vibrational frequencies. Nevertheless, frequencies are reported here to 1 cm^{-1} in order to show the sometimes small isotope shifts. The rationale is that each isotope will be affected to much the same extent by systematic errors in the force constant matrix so that the numerical precision in the calculated shifts may be as high as 1 cm^{-1}.

A recent[12] comprehensive study of vibrational modes in a variety of prototype molecules has led to a recommendation that frequencies calculated with the 3-21G basis set be scaled by the multiplicative factor 0.89 to approximately correct for the combined effects of electron correlation and anharmonicity. This empirical scaling factor is adopted here in order to facilitate comparison of the calculations with experiment.

Results and Discussion

The totally symmetric normal modes that are candidates for observation by resonance Raman spectroscopy are illustrated in Figure 1 with their Wilson assignments and calculated frequencies. The vectors in the figure are scaled to represent the relative amplitudes of the nuclear displacements in each of the normal modes. To facilitate comparison with experiment, the calculated frequencies, scaled by the empirical factor of 0.89, are listed in Table I. A more complete discussion of the calculated equilibrium geometry and of all 30 of the calculated normal modes will be presented in a forthcoming publication.[5] This work will also include comparisons with the corresponding neutral species and with several other closely related

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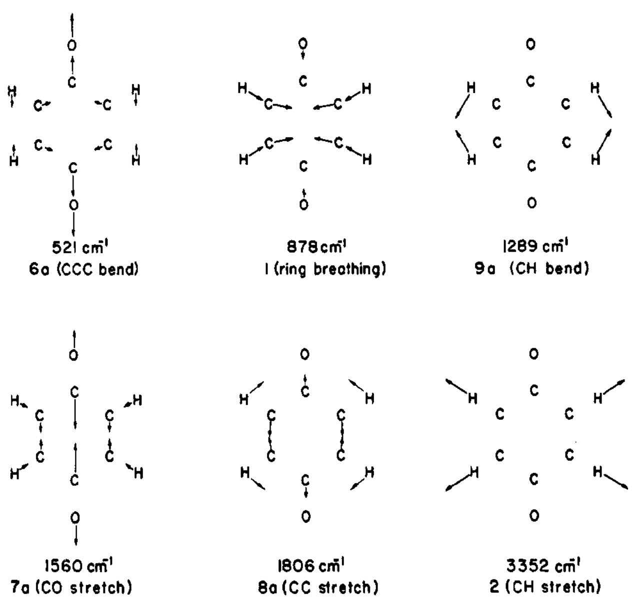

Figure 1. Calculated UHF/3-21G frequencies and normal modes for totally symmetric vibrations of *p*-benzosemiquinone radical anion.

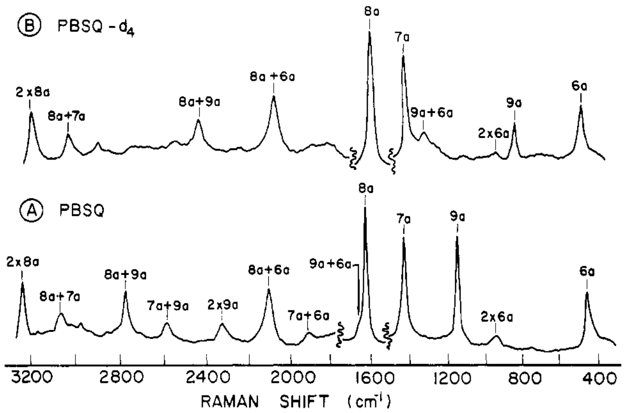

Figure 2. Raman spectra of (A) *p*-benzosemiquinone and (B) *p*-benzosemiquinone-d_4 radical anions. The 8a bands are recorded at a gain of 1/3. Radicals were produced by irradiating a N_2O-saturated 2 mM solution of the hydroquinone at pH ~11. Excitation was at 430 nm. The various bands, combination modes, and overtones are indicated by their Wilson assignments.

systems. Agreement between the frequencies observed for the protonated radical[3,4,13] and those given by these calculations is very good, giving additional convincing evidence that the assignments proposed earlier[3,4] are indeed correct. Agreement of the calculations with the isotope shifts reported below is even better than for the frequencies themselves. Only the CH bending and stretching modes should have large isotope shifts.

The Raman spectra of both the protonated and deuterated radicals, observed in the present study by excitation at 430 nm, are given in Figure 2. The signal-to-noise ratio obtained with the excimer pumped laser system and OMA detection is considerably improved over that obtained in our previous studies on the semiquinones.[3,4] In each case, four of the six totally symmetric vibrations are observable. The frequencies of the centers of each of those lines and their relative intensities are given in Table I. For the protonated radical the frequencies agree with those previously given[3,4,13] to within experimental error. Bands ascribable to the symmetrical ring breathing and CH stretching modes, which from the calculations should occur at ~800 and ~3000 cm^{-1}, do not appear in the spectra because they are not resonance enhanced, as we have discussed previously.[4] It should be noted that the band of the 9a vibration, which on deuteration is shifted to a 317-cm^{-1} lower frequency, is also much less resonance enhanced in the deuterated radical because the coupling with the C–C stretching vibration is considerably reduced. The line shapes are simple and for the most part can be approximated very well by a Lorentzian.

TABLE II: *p*-Benzosemiquinone Combination Bands and Overtones

	^{2}H		^{2}D	
	sum	obsd[a]	sum	obsd[a]
6a + 9a	1642	1650 (3)[b]	1324	1322 (18)
6a + 7a	1916	1914 (2)	1906	1900 (2)
6a + 8a	2101	2101 (14)	2077	2073 (14)
9a + 7a	2596	2590 (3)	2270	2270 (2)
9a + 8a	2781	2780 (10)	2441	2430 (3)
7a + 8a	3055	3050 (6)	3023	3016 (6)
6a + 6a	962	959 (3)	960	955 (3)
9a + 9a	2322	2324 (3)	1688	*a* (<1)
7a + 7a	2870	2860 (1)	2852	*a* (<1)
8a + 8a	3240	3238 (12)	3194	3193 (12)

[a] Intensities relative to 8a mode = 100 are given parenthetically. [b] Observed as a shoulder on the high-frequency side of 8a vibration. This shoulder is somewhat more well resolved in D_2O (cf. Figure 4).

It has also been possible to observe all of the simple combination bands and overtones except for the very weak overtones of the 7a and 9a vibrations in the deuterated radical. The observed frequencies, given in Table II, are for the most part as expected from the fundamentals, showing that there is very little anharmonicity in the lower vibrational levels of this radical. Combination bands involving the 7a mode (CO stretch), however, tend to be somewhat lower than expected from the fundamentals. Extensive examination of the spectrum of the protonated radical did not indicate any other bands which could be ascribed to nontotally symmetric modes although it is possible that the shoulder on the high-frequency side of the 8a vibration (at ~1650 cm^{-1}) could arise from this source indirectly. However, we tentatively assign this shoulder to the combination of the 6a and 9a vibrations expected at 1642 cm^{-1}. This shoulder is absent in the deuterated radical where the 6a and 9a combination is shifted to 1322 cm^{-1}.

A search for lines attributable to the 6% singly protonated radical impurity in the deuterated sample indicated only a very weak band at 1115 cm^{-1} that could possibly be due to this radical. This band corresponds to the CH bend in the partially deuterated radical. Because of the lower symmetry, 21 Raman active frequencies are expected but these should exhibit lower intensities than in the symmetrical radicals.

Absorption spectra for both the protonated and deuterated radicals obtained from the pulse radiolysis experiments are given in Figure 3. These were taken under conditions where the background concentration of *p*-benzosemiquinone was sufficiently low that the hydroquinone was quantitatively oxidized by the OH radicals produced in the water so that it was possible to determine the absolute extinction coefficients. A radiation chemical yield of 5.4 was assumed to apply to N_2O-saturated solutions at 0.2 mM hydroquinone.[14] Addition of *tert*-butyl alcohol showed that the H atom adducts do not contribute

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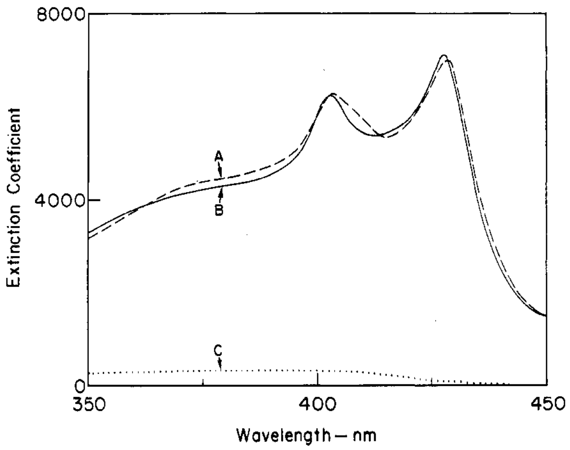

Figure 3. Absorption spectra of (A) *p*-benzosemiquinone and (B) *p*-benzosemiquinone-d_4 radical anions in aqueous solution at pH ~11 as observed in pulse radiolysis experiments (H atom contribution is given by C). Essentially the same features are observed in conventional spectrophotometric studies of the radical prepared by chemical oxidation. Deuteration of the radical largely removes the contribution observed for the protonated radical at 408 nm.

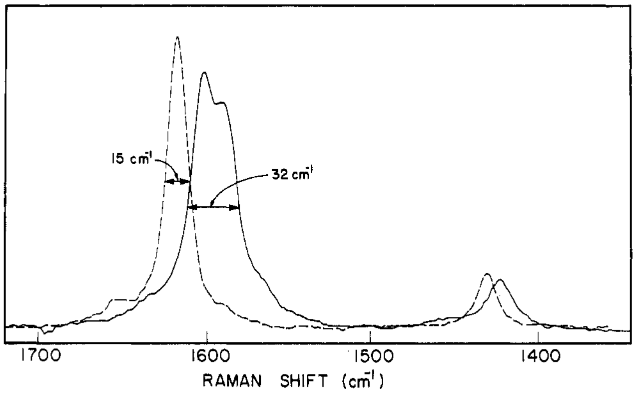

Figure 4. Raman spectrum of *p*-benzosemiquinone (dashed curve) and *p*-benzosemiquinone-d_4 (solid curve) as observed in D_2O. Excitation was at 430 nm. Spectra are displayed at comparable sensitivities. The protonated radical exhibits the two Lorentzian shaped lines of the 8a and 7a vibrations at 1621 and 1435 cm^{-1}. The first has a shoulder at 1650 cm^{-1} which is somewhat more well resolved than in H_2O. The complicated spectrum of the deuterated radical in the region of 1600 cm^{-1} shows that the ring stretching vibration (8a) is strongly perturbed by overlap with a nonresonance enhanced mode.

significantly, particularly above 420 nm. Complications by other reaction products on the time scale of these experiments should be absent. The spectra recorded by conventional spectrophotomery on air-oxidation samples show essentially the same features as in Figure 3, although the intensities could not be directly compared because of lack of information on the concentrations and deterioration with time which gives a product with a broad structureless background extending out past 600 nm.

Comparison of the absorption spectra of the protonated and deuterated radicals shows that the spectra are very similar with maxima at 427 and 403 nm in the former case and 426 and 402 nm in the latter. The separation of the two main peaks corresponds to a vibrational spacing of ~1410 cm^{-1}. As expected, the bands at 427 nm, which presumably correspond to a 0–0 transition, have essentially the same shape and amplitude in both radicals (extinction coefficients of 7050 and 7100 M^{-1} cm^{-1}, respectively, for the potonated and deuterated radicals) and are shifted by only ~0.5 nm. In the experiments with the Cary, the broad band at ~350 nm of Figure 3 is resolved into two very weak bands at 339 and 369 nm in the case of the deuterated radical. Somewhat more intense bands are observed in this region for the halogenated derivatives of benzosemiquinone.[4]

The most pronounced effect of deuteration is the simplification of the structure of the absorption spectrum in the 400–410-nm region. Comparison of the two spectra clearly shows that the spectrum of the protonated radical is complicated by a small but noticable contribution from a band in the region of 408 nm. We assume by analogy with the results from the Raman experiments that this band is due to the 9a vibration in the excited state and, as the result of deuteration, is shifted to a longer wavelength and reduced in intensity. As a result, the band at 402 nm becomes rather more well-defined in the deuterated radical where the vibrational spacing in the excited state can be measured from the absorption spectrum with fair accuracy (1410 ± 10 cm^{-1}). This spacing is considerably lower than the 1620-cm^{-1} frequency noted for the C–C stretch in the ground state, but similar to that of the CO stretch.

While the ESR experiments on hydroquinone-d_6 qualitatively identify $C_6D_4O_2^{-}\cdot$ as the principal radical produced in the oxidation and show that the only significant radical impurity present is 6% $C_6HD_3O_2^{-}\cdot$ they provide no new structural information on the semiquinone. They do, however, show that the ring deuterons of the radical do not readily exchange with the protons of the water. The ESR spectrum of the deuterated radical is centered at $g = 2.00457 \pm 0.00001$ and consists of a nine-line pattern corresponding to four equivalent atoms with $a_D = 0.359 \pm 0.002$ G. The g factor is within experimental error identical with that of the protonated radical and the hyperfine constant is as expected, i.e., 2.36 G/6.514 = 0.362 G. Unfortunately, the lines of the $C_6HD_3O_2^{-}\cdot$ mask the region where the ^{13}C satellites of the fully deuterated radical are expected so that no ^{13}C hyperfine data are available from these experiments. The parameters measured for the singly protonated radical are $g = 2.00457 \pm 0.00002$, $a_H = 2.40 \pm 0.01$ G, and $a_D = 0.359 \pm 0.002$ G.

It is noted in Figure 2 that the Raman line of the ring stretching (8a) vibration is considerably broader in the deuterated than in the protonated radical. Recordings taken with a spectrometer slit of 0.2 mm, where the band pass of the instrument (~5 cm^{-1}) does not contribute significantly to the observed widths, give widths (fwhm) of 17 and 31 cm^{-1}, respectively, for the signals of the deuterated radicals. Similar widths were observed by exciting the Raman emission at 440 nm. In both cases the other fundamental vibrations have widths of 15–20 cm^{-1} so that the effect is very specific to the 8a vibration of the deuterated radical. The line shape of the 8a vibration of the protonated radical is very near to a pure Lorentzian (see Figure 4), whereas that of the deuterated radical, while exhibiting no resolvable structure in H_2O, is clearly more complex. The integrated area for the deuterated radical was found to be a factor of ~1.6 greater than that for the protonated radical even though the experimental conditions were identical.

In D_2O two contributions of nearly equal intensity are partially resolvable at 1592 and 1603 cm^{-1}, as is illustrated in Figure 4. While the Raman line of the protonated radical at 1620 cm^{-1} is very slightly narrower in D_2O the difference does not appear to be sufficient to resolve the structure evident in the figure. Rather, the comparison between the two solvents is more complicated, with the contribution at 1603 cm^{-1} in D_2O appearing to have been shifted from a very slightly lower frequency in H_2O. This peak is roughly where the 8a vibration of $C_6HD_3O_2^{-}\cdot$ is expected but the intensity is far too great to be attributed to this species (the ESR experiments show only a 6% contribution) unless the band is enhanced considerably more than for the fully deuterated radical. There is no precedent for such an effect. The spectra of Figure 4 were recorded under comparable radical concentrations and detector response. The considerably greater integrated intensity for the deuterated radical is readily evident. This aspect makes it reasonably clear that there is an important contribution in the deuterated case which is absent in the protonated case and, at this point, one can only speculate as to the source of this extra intensity. A strong possibility is that a band which normally does not exhibit significant intensity is considerably enhanced because of overlap with a 8a vibration, as occurs, for example, in the case of benzene.[15] The theoretical calculations show no other fundamentals in the region of 1600 cm^{-1} so one must explore the overtone and combination frequencies. A likely candidate is combination of the C–H bending and ring breathing modes (9a + 1) which should have a frequency very near to 1600 cm^{-1} (see below) in the deuterated radical but ~1840 cm^{-1} in the protonated case. These modes both have the same symmetry as the 8a vibration so that Fermi resonance can play an important role.

The situation is obviously very complex and critically dependent on details of the vibrational spacings. The theoretical calculations (with the 0.89 scaling factor included) indicate only two other candidates among the nonsymmetric vibrations anywhere near 1600 cm^{-1}. One is a combination of B_{3g} modes calculated to be at 608 + 1002 = 1610 cm^{-1}. Because the scaled frequencies are calculated uniformly low in all cases that comparison with experiment is possible in this system the combination band would very probably be somewhat higher and would not be close enough to participate in a Fermi resonance. Another possibility is a combination of B_{2g} modes calculated at 671 + 911 = 1582 cm^{-1}. While overlap with the 8a mode is more likely here on the basis of frequency the B_{2g} modes involve out-of-plane vibrations and are unlikely to be resonance enhanced since the excitation polarization is in the plane of the molecule. The overtone of the A_g ring-breathing mode calculated at 1510 cm^{-1} and the combination of B_{1u} modes at 663 + 837 = 1500 cm^{-1} would seem too far away in frequency to be resonable candidates. For these reasons, we tentatively assign the feature to the combination band calculated at 755 + 829 = 1584 cm^{-1} undergoing a Fermi resonance with the band calculated at 1574 cm^{-1} giving two observed bands centered at 1597 cm^{-1}.

Registry No. *p*-Benzosemiquinone radical anion, 3225-29-4; *p*-benzosemiquinone-d_4 radical anion, 57413-83-9.

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Correlations between Average Atomic Numbers and Spectroscopic Constants of Diatomic Molecules

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New linear correlations between dimensionless ratios of ground-state spectroscopic constants of diatomic molecules, AB, and logarithms of various averages of the atomic numbers, Z_A and Z_B, of the constituent atoms have been found to hold with a fair degree of accuracy within colpair families (sets of diatomics containing one atom from each of a specified pair of columns of the periodic table). These may be thought of as quantitative extensions of a previous suggestion of Calder and Ruedenberg that the Dunham parameters a_1 and a_2 are constant within a colpair family. The electronic kinetic energy normalization model using the T-normalized Rydberg representation of the kinetic energy has been shown to predict the general form of these correlations. This model also provides a justification for an empirical correlation of Hefferlin and co-workers, and suggests some additional correlations. Implications of the correlations for the parameterization of the simple bond charge and perfectly following densities models of molecular vibrations are examined.

Introduction

It remains a significant goal of theoretical chemistry to find simple relationships between spectroscopic constants of diatomic molecules and properties of the constituent atoms. A number of relationships of varying degrees of generality are known.[1] Some[2-6] of these correlations are purely empirical ones while others are based upon simple models of molecular vibrations such as the simple bond charge (SBC) model,[7] the perfectly following densities (PFD) model,[8] and the kinetic energy normalization (KEN) model.[9] Correlations derived from such models provide a check of their validity and increase our under-

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