and in liquids, whereas the rotation barriers are generally 1-2.3 kcal/mol lower in the gas phase. Any solvent increases the rigidity of the amide bond.

Registry No. DMA, 127-19-5; DMCCl, 79-44-7; DMCF, 431-14-1; DMTFA, 1547-87-1; DIA, 759-22-8; DEF, 617-84-5; DMTA, 631-67-4.

Supplementary Material Available: The chemical shifts and the coupling constants of the amides in the gas phase are given in Tables SI and SII. Calculated and experimental spectra are reproduced in Figures S1 to S6 (13 pages). Ordering information is available on any current masthead page.

Resonance Raman Investigation of the π^* Antibonding Distribution in Excited Triplet Aqueous *p*-Benzoguinone

R. Rossetti, S. M. Beck, and L. E. Brus*

Bell Laboratories, Murray Hill, New Jersey 07974 (Received: December 28, 1982)

The time-resolved resonance Raman spectra of triplet p-benzoquinone in water have been investigated at 266, 315, 355, and 416 nm. Recent improvements in the apparatus are described. The C==C ring stretch (Wilson's 8a) and the symmetric C=O stretch are tentatively identified, using the isotopic shift for ring deuteration and comparison with the semiquinone radical anion. The symmetric carbonyl stretch at 1496 cm⁻¹ is unusally high for an n- π^* excited state. The C=C ring stretch at 1552 cm⁻¹ is unusually low for a quinoid type species. These results indicate that there is π^* antibonding density on the ring as well as on the carbonyl groups. Comparison is made with previous $S_0 \twoheadrightarrow T_1$ vibronic electronic absorption studies in neon matrices.

Introduction

Transient resonance Raman spectroscopy has become a diagnostic approach to liquid-phase kinetics that offers distinct advantages in understanding chemical reactions. The method yields direct structural information about short-lived species, and often distinguishes among multiple and similar intermediate species having overlapping optical spectra.

We describe transient Raman studies on the lowest $n-\pi^*$ triplet state of p-benzoquinone. This state has been the subject of recent experimental and theoretical investigations,¹⁻⁴ centering on the facts that (1) this "state" is actually two nearly degenerate ($\Delta E \sim 10 \text{ cm}^{-1}$) n- π^* states in the isolated molecule, and (2) the π^* antibonding density seems to be delocalized onto the ring. The near-degeneracy results from an extremely weak interaction between the n orbitals on the two carbonyl oxygens. Potential vibronic coupling between these two states raises unresolved questions about the vibronic structure.

We observe the *solvated* excited state. In water, solvation will be a strong effect, as the excited state is a strongly oxidizing species with a calculated redox potential slightly below that necessary to oxidize water to the OH radical.⁵⁻⁶ There should be a charge transfer interaction which could affect the vibronic structure.

We have earlier shown that one 416-nm nanosecond pulse can excite aqueous p-benzoquinone (BQ) to the T_1 state, and generate the resonance Raman spectra of that state.⁵ We now report higher resolution spectra in the 1600-cm⁻¹ region, and attempt a vibrational assignment for BQ- h_4 , BQ- d_4 , and the methyl derivative MeBQ (Toluquinone). Our purpose is to understand the changes in

electron distribution in the excited state, as reflected in the changes in vibrational frequencies when compared with the S_0 ground state and other carbonyl species.

Experimental Section

We have incorporated several modifications into our previously described apparatus.⁷ As shown in Figure 1, there are two independently controlled ND:YAG 10-Hz lasers. Probe wavelengths necessary for a specific experiment are produced by Raman shifting the YAG harmonics in hydrogen or methane, or by pumping a dye laser with the YAG laser.

The colinear laser beams are brought to an approximate line focus in a flowing solution stream ($\sim 2 \text{ mm diameter}$). The beams are physically above the collection lens in the figure, and propagate in a downward direction to the interaction region. In the stream the beams propagate at an angle of $\simeq 12^{\circ}$ with respect to the Raman optical collection axis. Raman scattered light is collected in a near backscattering geometry. This arrangement utilizes the depth-of-field of the collection lens to increase the Raman signal.

In the 416-nm experiments, 10-ns, 1-mJ pulses are brought to a line focus at peak fluxes of $\sim 10^7 \, \mathrm{W/cm^2}$. As the absorption coefficient of ground electronic state (S_0) BQ is low at 416 nm ($\simeq 20 \text{ L/(mol·cm)}$), only about 1% of BQ molecules are excited per pulse.

The triple spectrograph consists of an Instruments SA prototype subtractive dispersion double premonochromator, and an Instruments SA HR-640 spectrograph as the third stage. The subtractive dispersion double has two planar ruled gratings on a common shaft, yielding a uniform spectral bandshape. The 0.64-m third stage provides higher spectral resolution than previously used, in order to observe small shifts and line shape changes. With an ultraviolet (3600 L/mm) grating, the instrumental reso-

Trommsdorf, H. P. J. Chem. Phys. 1972, 56, 5358.
 Lichtenbelt, J. H.; Wiersma, D. A. Chem. Phys. 1978, 34, 471.
 Goodman, J.; Brus, L. E. J. Chem. Phys. 1978, 69, 1604.

Martin, R. L.; Wadt, W. R. J. Phys. Chem. 1982, 86, 2382.
 Beck, S. M.; Brus, L. E. J. Am. Chem. Soc. 1982, 104, 1103.
 Beck, S. M.; Brus, L. E. J. Am. Chem. Soc. 1982, 104, 4789.

⁽⁷⁾ Beck, S. M.; Brus, L. E. J. Chem. Phys. 1981, 75, 4934.



Figure 1. Schematic diagram of the apparatus. The beam from the Raman probe laser can either pump the dye laser or undergo stimulated Raman processes in H₂ gas.

lution is $\simeq 6 \text{ cm}^{-1}$ (fwhm) for a 266-nm Raman probe wavelength; with a visible grating, the instrumental resolution is $\simeq 5 \text{ cm}^{-1}$ at 416 nm. The principal limiting factor is the 4–5 channel (fwhm) spatial resolution of the PAR 1420 intensified reticon.

BQ- d_4 was prepared from perdeuteriohydroquinone by method 2 of Vogel, involving reaction with sodium chlorate in the presence of vanadium pentoxide.⁸ Perdeuteriohydroquinone was synthesized by exchanging hydroquinone in a 20% DCl in D₂O solution for about 24 h at 100 °C, in a fashion similar to that described by Charney and Becker.⁹ BQ- h_4 , BQ- d_4 , and MeBQ were purified by sublimation.

Observations

Ground State. The type and intensity of the vibrational modes observed depends upon the nature of the electronic transition in resonance with the Raman probe wavelength. In principle, a more complete structural picture appears when spectra obtained in resonance with several different electronic transitions are combined. Our previous results at 416 nm are in resonance with the lowest electronic transitions of both the ground state S_0 and the lowest triplet $T_{5.6}^{5.6}$ We have thus explored the ultraviolet probe wavelenghts 266, 315, and 355 nm in an attempt to come into resonance with other transitions of both species.

The S₀ state exhibits a weak $n-\pi^*$ transition ($\epsilon \sim 20$ L/(mol·cm)) near 420 nm, and a stronger $\pi-\pi^*$ transition ($\epsilon \sim 3000$ L/(mol·cm)) near 290 nm.¹⁰ As previously reported, and as shown in Figure 2, the S₀ state shows one strong 416-nm resonance Raman line in the 1600-cm⁻¹ region at 1676 cm⁻¹. This line in BQ-d₄ is at 1664 cm⁻¹. We now find that the 266-, 315-, and 355-nm resonance Raman spectra show this same single line, as exhibited in Figure 3. At 416 nm this line shows parallel polarization ($\rho \simeq 0.5$) as expected for a totally symmetric mode.

In BQ there are two a_g fundamentals in the 1600-cm⁻¹ region. These are the C=C ring stretch (Wilson's 8a), and the symmetric carbonyl C=O stretch. In S₀ these modes are nearly degenerate and show varying degrees of inter-



Figure 2. Pulsed, 416-nm resonance Raman spectra of a 3×10^{-2} M aqueous benzoquinone solution. S₀ refers to the ground state, and T₁ to the lowest triplet state. QH· refers to the neutral semiquinone radical. Isotopic shifts are shown. The 1495-cm⁻¹ band in BQ- h_4 may correspond to the indicated shoulder in BQ- d_4 .



Figure 3. The 266-nm resonance Raman spectra of aqueous benzoquinone (pH \simeq 5). Only S_0 lines are observed.

action as a function of environment. Dunn and Francis place these modes at 1687 and 1660 cm⁻¹ in BQ- h_4 , and at 1650 and 1643 cm⁻¹ in BQ- d_4 , in molecular crystals.¹¹

One method to aid in assignment of these modes in the solvated species is via the isotopic shift for ring deuteration. The ring stretch should be more sensitive to ring deuteration, and in fact the crystal data show a 37-cm⁻¹ shift for the C=C stretch and a 17-cm⁻¹ shift for the C=O stretch. In benzenoid rings the 8a isotopic shift is typically larger than 37 cm⁻¹. Our Raman transition shows a 12-cm⁻¹ shift. We thus tentatively identify this line as the a_g C=O stretch in the solvated S_0 state; the small isotopic shift suggests it is not strongly mixed with the ring stretch. The symmetric C=O stretch also dominates the 1600-cm⁻¹ region Raman spectrum at longer (Ar⁺ laser) wavelengths.¹¹

The two $n-\pi^*$ transitions at 420 nm, and the $\pi-\pi^*$ transition at 290 nm $({}^{1}A_{g} \rightarrow {}^{1}B_{3g})$, are symmetry forbidden in D_{2h} .¹⁰ The principal oscillator strength in the $n-\pi^*$ transitions has been analyzed as borrowed from some higher lying ${}^{1}A_{g} \rightarrow {}^{1}B_{1u}$ transition, polarized along the carbonyl axis.¹² There is an extremely strong ${}^{1}A_{g} \rightarrow {}^{1}B_{1u}$ $\pi-\pi^*$ transition near 200 nm.¹⁰ Totally symmetric modes are not enhanced in resonance with electronically forbid-den transitions, in the lowest order Raman theory. There is a weak, higher order A' term which may enhance the a_{g} C=O stretch in vibronically allowed transitions, if there

⁽⁸⁾ Vogel, A. I. "Practical Organic Chemistry"; Longman: London, 1978; 4th ed, p 788.

 ⁽⁹⁾ Charney, E.; Becker, E. D. J. Chem. Phys. 1965, 42, 910.
 (10) Bunce, N. J.; Ridley, J. E.; Zerner, M. C. Theor. Chim. Acta (Berlin) 1977, 45, 283.

⁽¹¹⁾ Dunn, T. M.; Francis, A. H. J. Mol. Spectrosc. 1974, 50, 1.

⁽¹²⁾ Hollas, J. M. Spectrochim. Acta 1964, 20, 1563.



Figure 4. The 416-nm resonance Raman spectra, as in Figure 2. The BH- h_4 solution contains 8% methanol, and the BQ- d_4 solution contains 10% methanol. QH- isotopic shifts are shown.

TABLE I: 416-nm Resonance Raman Spectra of Triplet **Benzoquinone**^a

	triplet		
$\mathbf{S}_{0}, \mathbf{h}_{4}$	h ₄	d ₄	mode
445	455 (7) 901 (0.7) 947 (0.7)	453	CCC 6a
1160	1163 (6) 1360 (0.5)	843	C—H wag 9a
$\begin{array}{c} 1660\\ 1674 \end{array}$	1496 (1) 1554 (9) 2003	shoulder? 1529 1976	sym C=O C=C 8a

^a Entries are peak frequencies in cm⁻¹. Numbers in parentheses are relative peak heights. The S_0 data for comparison refer to single crystals (ref 11).

is a displacement along this mode in the state in reso-Without a detailed excitation spectrum, we nance.13 cannot determine if the C=O Raman activity comes directly from the far ultraviolet, or from an A' type term.

The Triplet State and the Semiquinone Radical. As previously reported, and as shown in Figures 2 and 4, pulsed 416-nm excitation also shows transient spectra of the photoproducts BQ(T) and BQH (the protonated semiquinone radical) produced by the same optical pulse. We have also previously shown that pulsed 266-nm excitation produces BQ(T) and semiquinone species, via observations with a delayed 416-nm probe pulse. The fact that our ultraviolet pulsed Raman spectra do not also show these photoproducts indicates that these species have low Raman cross sections at these probe wavelengths. Thus unfortunately we have not gained any new information by going to ultraviolet probe wavelengths. To our knowledge the corresponding ultraviolet transient absorption spectra of BQ(T) and BQH have not been investigated.

Table I lists the observed BQ(T) resonance Raman transitions, obtained from Figure 2, Figure 4, and other spectra. The triplet shows a strong, broad line at 1554 cm⁻¹ with an isotopic shift of 25 cm⁻¹ in BQ- d_4 . This shift is larger than expected for a pure symmetric C=O motion. BQ- h_4 also shows a weak second line at 1496 cm⁻¹ in Figure 2; this line is not apparent in BQ- d_4 . These lines, as do the semiquinone lines, all show parallel polarization.

The 28-cm⁻¹ (fwhm) width of the 1554-cm⁻¹ line is a factor of two larger than that of the other BQ(T) lines, and the S_0 line. This width might suggest that this transition has two (or more) unresolved components, or that the corresponding mode is especially sensitive to solvation. The width is unchanged in BQ- d_4 .

With limited data, and without a force field calculation, we must consider indirect arguments. Triplet states are often similar to the corresponding negative anion (BQ^{-}) ; in both species the same antibonding π^* orbital is populated. The 420-nm triplet-triplet transition is very similar in shape and intensity to the lowest absorption of BQ; in a simple approximation both electronic transitions are the lowest $\pi - \pi^*$ transition of a quinone species with 9 π electrons. Tripathi has analyzed the 420-nm region resonance Raman spectra of substitued BQ⁻ species in detail. The C=C line is invariably strongest, with the C=Otransition often 1/10 as strong. In BQ⁻ itself, the C==C line is at 1620 cm⁻¹, while the C=O line (1/3 as strong)is at 1435 cm^{-1.14,15} In the protonated species BQH, the C=C line is still strongest and remains near 1620 cm^{-1.6} The apparent C=O transition, now localized on one end, increases in intensity and moves to 1515 cm⁻¹. The partial carbonyl bond in phenoxy radical also appears to be near 1515 cm⁻¹.¹⁶

The isotope shift of the 1554 cm⁻¹ line in BQ(T) suggests that the corresponding mode has at least partial C=C character. As we shall see in a subsequent paragraph, "C=C" mode in BQH has about the same isotopic shift. We suggest then that the strong 1554-cm⁻¹ line is principally C=C motion, and the weak 1495-cm⁻¹ line is principally C=O motion, in BQ- h_4 . If so, the 1495-cm⁻¹ line would be expected to have an isotopic shift smaller than 27 cm⁻¹. In BQ- d_4 this line may lie under the wing of the strong 1529-cm⁻¹ line, as in Figure 2.

We emphasize that our discussion applies to the solvated excited state. A high-resolution spectrum of the isolated molecule in vacua might show a more complex vibronic spectrum in the 1600-cm⁻¹ region, as there are three nearby modes (including the asymmetric C=O stretch) in an essentially doubly orbitally degenerate electronic state.

An alternative method of observing these modes is via the vibronic structure in the weak $S_0 \rightarrow T_1$ electronic absorption. We have previously attempted this for isolated BQ in neon matrices at 4 K.³ These vibronic transitions lie in a region of stronger $S_0 \rightarrow S_1$ absorption. There is a weak, unassigned line (labeled XI) at 1487 cm⁻¹ with an isotopic shift in BQ- d_4 of only 6 cm⁻¹. This line could well be the symmetric C=O stretch, and correspond to our resonance Raman line at 1496 cm⁻¹. This possible assignment of the matrix data was first suggested by Martin and Wadt.³ There is also a second unassigned line at 1600 cm^{-1} (labeled XII) with an isotopic shift of 18 cm^{-1} . The relationship of this line, if any, to our strong, broad Raman feature at 1554 cm⁻¹ is uncertain. The Franck-Condon factor for the C=C stretch in the $S_0 \rightarrow T_1$ absorption should be small as the frequency decrease in T_1 is relatively small.

Figures 2 and 4 also show weak lines previously assigned to semiguinone radicals, formed in the oxidation of water by excited BQ. It was originally shown by transient absorption spectroscopy that the semiquinone radical spectrum is present after the BQ(T) spectrum decays on the approximately 500-ns time scale.¹⁷ Methanol oxidizes more readily than water, and BQH- lines grow relative to BQ(T) lines when methanol is added, as in Figure 4.6 This technique allows us to obtain the 1600-cm⁻¹ region spectra of BQH deuterated on the ring. In BQH (h_4) the two lines

⁽¹⁴⁾ Tripathi, G. N. R. J. Chem. Phys. 1981, 74, 6044.
(15) Tripathi, G. N. R.; Schuler, R. H. J. Chem. Phys. 1982, 76, 2139.
(16) Beck, S. M.; Brus, L. E. J. Chem. Phys. 1982, 76, 4700.
(17) Ronfard-Haret, J. C.; Bensasson, R. V.; Amouyal, E. J. Chem. Soc., Faraday Trans. 1 1980, 76, 2432.

⁽¹³⁾ Ziegler, L. D.; Albrecht, A. C. J. Chem. Phys. 1979, 70, 2644.

are at 1619 and 1515 cm⁻¹, while in the d_4 species the lines appear at 1591 and 1492 cm^{-1} .

Methylbenzoquinone. In order to investigate the possible role of symmetry in these spectra, we obtained the 416-nm spectra for MeBQ. The data are quite smaller to those of Figure 2 for BQ, with the principal change being that the T_1 transitions are weaker in comparison with those of S_0 and BQH at a given 416-nm flux. The S_0 line occurs at 1676 cm⁻¹, and the principal T_1 line is at 1559 cm⁻¹. The T_1 spectra are sufficiently weak that we could not observe the analogous line to 1495 cm⁻¹. A weak, low symmetry perturbation such as ring methylation has little effect on the spectra.

Electronic Structure in BQ(T)

An isolated S_0 carbonyl group typically has a C=O frequency near 1700 cm⁻¹, and a $n-\pi^*$ excited-state frequency of 1000-1100 cm⁻¹. In BQ⁻ the symmetric C==O frequency is 1435 cm^{-1} , and we have tentatively placed it at 1496 cm^{-1} in BQ(T). The C=O frequency decrease in the excited BQ(T) state is only a fraction of that expected for an isolated carbonyl group. If this assignment is correct, the C=O frequency in BQ(T) is the highest ever observed in a carbonyl $n-\pi^*$ excited state.

BQ(T) in this tentative assignment shows a lower C=C frequency, and a higher C=O frequency than BQ^{-} . This result suggests there is relatively more antibonding π^* character on the ring in BQ(T) than in BQ^{-} . In comparing S_0 with T_1 , the C=C (8a) frequency has dropped by $\simeq 100$ cm⁻¹, while the symmetric C=O frequency has dropped by $\simeq 180 \text{ cm}^{-1}$. There is substantial antibonding charactr on the C=O groups as well as on the ring. In the lowest $^{3}n-\pi^{*}$ state of the similar D_{2h} species pyrazine, the π^{*} density is necessarily entirely on the ring. In this case, the 8a stretch drops from 1584 cm⁻¹ in S_0 to 1222 cm⁻¹ in T_1 .¹⁸

Acknowledgment. We thank Dr. G. N. R. Tripathi for an interesting discussion of this problem.

Registry No. p-Benzoquinone, 106-51-4; D₂, 7782-39-0.

(18) Herzberg, G. "Electronic Spectra and Electronic Structure of Polvatomic Molecules"; Van Nostrand-Reinhold: Princeton, N.J., 1966.

Numerical Simulation of the Long-Term Performance and Corrosion of **Photoelectrochemical Cells**

H. Flaisher and R. Tenne*

Department of Plastics Research, The Weizmann Institute of Science, Rehovot 76100, Israel (Received: March 15, 1982; In Final Form: September 23, 1982)

A computer program which simulates the long-term operation of a photoelectrochemical cell (PEC) has been devised by using the basic chemical reactions which are supposed to occur at the surface of the semiconductor electrode. The model takes into account the buildup of a top passivating layer. The rate constants for these reactions were derived implicitly by varying them until the results of the model were comparable to those obtained experimentally for the CdSe/polysulfide photoelectrochemical cell. Once these constants were found, the program was used to simulate experimental curves of efficiency as a function of the cell parameters and time. The ratio of peak photocurrent and steady-state photocurrent was evaluated as well. Effects of solution concentration, incident light intensity, and surface roughness (e.g., by photoetching) were all observed by using the model. These results are in qualitative agreement with many independent experimental observations. It is demonstrated that for a given electrode, when the rate of hole transfer into the electrolyte is increased (i.e., increased quantum vield), the rate of the electrode deactivation decreases in accordance with experimental observations.

Introduction

Due to the relatively high cost of producing solid-state solar cells, various alternatives to these devices are being sought. One of these substitutes is the photoelectrochemical cell (PEC) in which the p/n junction is replaced by a semiconductor (p or n)/electrolyte junction. Although these systems have some advantages over the conventional solar cell, they still have major shortcomings, such as their instability caused by reactions between the electrolyte and the surface of the semiconductor. It is therefore useful to try to predict the extent of electrode stability as a function of parameters such as illumination intensity, electrolyte concentration, etc., using a computer model. In particular, the effect of surface roughness on the performance and stability of the PEC is investigated in detail. This model pertains mainly to the CdSe/polysulfide PEC for which many experimental results have been gathered in the last few years. The algorithm of and results obtained by using the model will be described here.

Theory and Assumptions

The model is based generally on the arguments presented in ref 1, which are summarized here. It is assumed that the semiconductor is an n-type, binary compound (AB) and that the photoelectrochemical cell is operated in such a way that the electrolyte undergoes no net chemical change (i.e., only electricity is produced). The charge-transfer species in the electrolyte (C⁻) is assumed to be capable of being oxidized by one hole only.

(Capacity measurements² indicate that monovalent ions (HS⁻) are adsorbed on the surface of CdS in sulfide solution.) Although the oxidation of a sulfide ion by photo-

⁽¹⁾ R. Tenne, D. Lando, N. Müller, and Y. Mirovsky, J. Electrochem. Soc., 130, 852 (1983).

^{(2) (}a) T. Inoue, T. Watanbe, A. Fujishima, and K. Honda, Bull. Chem. Soc. Jpn., 52, 1243 (1979); (b) D. S. Ginley and M. A. Butler, J. Appl. Phys., 48, 2019 (1977); (c) H. Minoura, M. Tsuiki, and T. Oki, Ber. Bunsenges. Phys. Chem., 81, 588 (1977). (3) W. W. Gärtner, Phys. Rev., 116, 84 (1959).