cm^{-1}, respectively. For the N-deuterated uracil, the frequency of the band discussed above is almost the same as that of ordinary uracil, but for N-deuterated adenine and cytosine the frequencies are red shifted. The amount of red shift is smaller than that expected by a purely -N-D vibration. If this red shift was due to the deuteration of nitrogen atoms of the ring, a similar red shift would be expected for N-deuterated uracil, too. Thus, the slight red shift for N-deuterated adenine and cytosine is due to the mass effect of deuterating the amino group of these compounds. Uracil does not have an amino group; hence the strong band at 804 cm^{-1} in its SERS spectrum is due purely to a ring vibration, but the strong bands in the SERS spectra of adenine and cytosine at 739 and 801 cm^{-1}, respectively, are due to a ring vibration with some contribution from the amino group vibration.

This study coupled with previous ones indicates that SERS spectra may yield rather detailed information regarding the disposition and mode of bonding of molecules adsorbed on appropriate metal surfaces.

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Registry No. OABA, 118-92-3; MABA, 99-05-8; glycine, 56-40-6; α-alanine, 56-41-7; β-alanine, 107-95-9; 6-aminocaproic acid, 60-32-2; adenine, 73-24-5; cytosine, 71-30-7; uracil, 66-22-8; *N*-deuterated adenine, 51581-02-3; *N*-deuterated cytosine, 41548-40-7; *N*-dueterated uracil, 20666-60-8.

Picosecond Time Resolved Raman Scattering Study of Hydrogen Abstraction by Triplet Excited Benzoquinone

R. Rossetti and L. E. Brus*

Contribution from AT&T Bell Laboratories, Murray Hill, New Jersey 07974.
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Abstract: The excited state photophysics and H atom abstraction reaction of triplet *p*-benzoquinone in mixed H_2O:alcohol solvents are investigated on the ≃20 ps time scale with time-resolved resonance Raman spectroscopy. The triplet is present within 20 ps, and its Raman spectrum is fully developed. It appears that vibrational relaxation is complete at this time. There is no H atom abstraction during the vibrational relaxation process under present conditions. Abstraction proceeds from the relaxed triplet on longer time scales, with a clear kinetic isotope in deuterated solvents. The results also demonstrate that spontaneous Raman pump and probe experiments, at high optical flux, can be performed on chemical transients in low concentration.

Picosecond time-resolved electronic absorption experiments[1] are now common and have been recently extended to the femtosecond scale.[2] These measurements, however, generally provide *kinetic* but not *structural* information about transient chemical species. Time resolved Raman spectroscopy, if feasible, can be a more useful probe, in the sense that the data provide direct (albiet partial) vibrational information, and often distinguish among similar species exhibiting overlapping optical spectra. Transient Raman scattering experiments invariably require electronic resonance enhancement of the scattering cross section. In several cases where extremely large enhancements are present (e.g., hemes, excited singlet *trans*-stilbene, and reduced methyl viologen), transient Raman experiments have been successfully extended from the nanosecond to the picosecond time scale.[3-8] In this paper the picosecond Raman method is used to investigate the mechanism of hydrogen atom abstraction by electronically excited *p*-benzoquinone. In this reactive system, the two transient species observed (triplet benzoquinone and semiquinone radical) exhibit comparatively modest resonance enhancements.[9]

There are several earlier nanosecond Raman studies on H atom abstraction by triplet excited benzoquinone (hereafter Q(T), see Figure 1).[10-12] Vibrationally relaxed, equilibrated Q(T) is reported to abstract an H atom from pure neutral water slowly ($\sim 10^{-7}$ s) at room temperature.[13] Q(T) before reaction must be strongly hydrogen bonded. In alcohol:water mixtures the abstraction reaction is accelerated. In pure water, sequential two-photon absorption leads to fast abstraction. We have previously suggested that some abstraction may occur during the (fast) vibrational relaxation following single photon excitation at 416 nm.[10,11] Thus, it is interesting to directly observe Q(T) and possible reaction products on a shorter time scale.

An understanding of the picosecond Raman data requires comparison with and extension of the earlier nanosecond data. The basic experiment uses single 416-nm pulses to create transient species (Q(T) and semiquinone radical QH) and generate their electronic resonance Raman spectra within the pulse time width. The nanosecond Raman apparatus produces pulses of ≃8 ns width, while the picosecond apparatus produces pulses of ≃20 ps. These pulse widths define the effective time scales of the experiments.

The picosecond peak flux on the solution is 10^{10}-10^{11} W/(cm^2·s), several orders of magnitude higher than in nanosecond Raman experiments. We shall demonstrate that, at least in this chemical system, the same resonance Raman scattering and photochemical processes occur as at lower fluxes in the nanosecond experiments.

Observations

The nanosecond laser system, picosecond laser system, and detection system have been previously described.[8,12] In these

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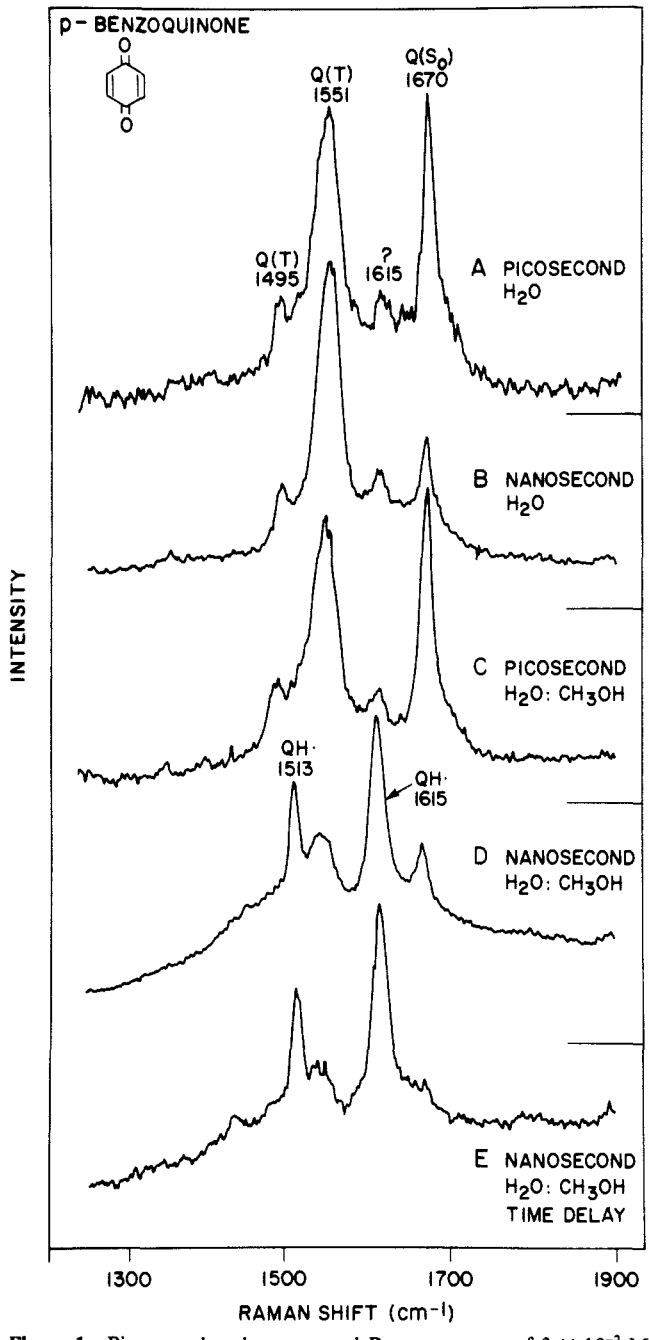

Figure 1. Picosecond and nanosecond Raman spectra of 3×10^{-2} M benzoquinone solutions at pH ~5 as described in the text. The instrumental resolution (fwhm) is ≃5 cm^{-1}. Methanol lines have been subtracted when necessary.

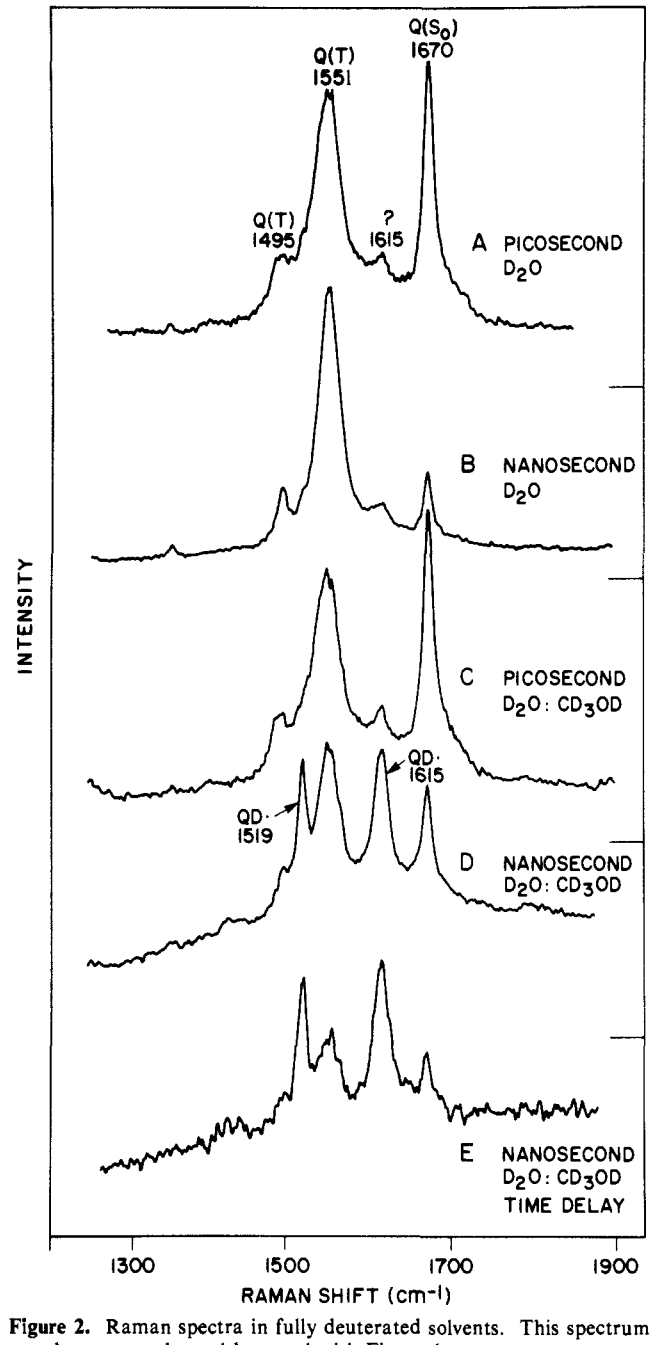

Figure 2. Raman spectra in fully deuterated solvents. This spectrum may be compared panel by panel with Figure 1.

present experiments, the same flowing solution stream and optical detection apparatus are used for both nanosecond and picosecond experiments. We have carried on experiments in both protonated and deuterated solvents in view of a possible kinetic isotope effect in the abstraction reaction. Figures 1 and 2 give the H and D solvent spectra, respectively; these spectra may be compared panel by panel.

In water at pH 5, the previously assigned nanosecond Raman spectra in the 1600-cm^{-1} region show a narrow S_0 (ground state) line at 1670 cm^{-1} and two broad Q(T) lines at 1550 and 1495 cm^{-1}. The two Q(T) lines grow in intensity in comparison with the S_0 line as the laser pulse fluence increases, as previously described. Q(T) appears via intersystem crossing after absorption of a 416-nm photon. Excited state benzoquinone has initially 0.7 eV of excess vibrational energy; it quickly thermalizes and a second 416-nm photon from the same pulse generates its Raman spectrum.

Addition of about 10% alcohol to the solvent, at constant fluence, produces two additional QH· resonance Raman lines (1615 and 1513 cm^{-1}) as shown in Figure 1D as compared with Figure 1B. These lines appear at the expense of the strong 1550 cm^{-1} Q(T) line. QH· is a reaction product of Q(T) with the solvent.

It is vibrationally relaxed Q(T) which reacts with alcohol to give QH. This conclusion is established by a comparison of traces C and D in Figures 1 and 2. The multichannel optical detection system has a ~10 ns electronic gate that is synchronized with the optical pulse. In trace D the gate is delayed 5 ± 2 ns, so that Raman scattering is collected only during the tail of the optical pulse. Here we see that the QH· lines increase in real time at the expense of the Q(T) and S_0 lines. This result shows that QH· and relaxed Q(T) do not have the same time dependence, which would have been the case if QH· were produced during the vibrational relaxation of Q(T). We conclude that equilibrated Q(T) is reacting with alcohol on the time scale of a few nanoseconds under these conditions.

The evolution of Q(T) to form QH· is also seen in the low-frequency Raman data. In H_2O and D_2O, there is one strong transition in the 130–600 cm^{-1} spectral region, at 447 cm^{-1} in both solvents, as seen in Figure 3A. The fluence dependence indicates

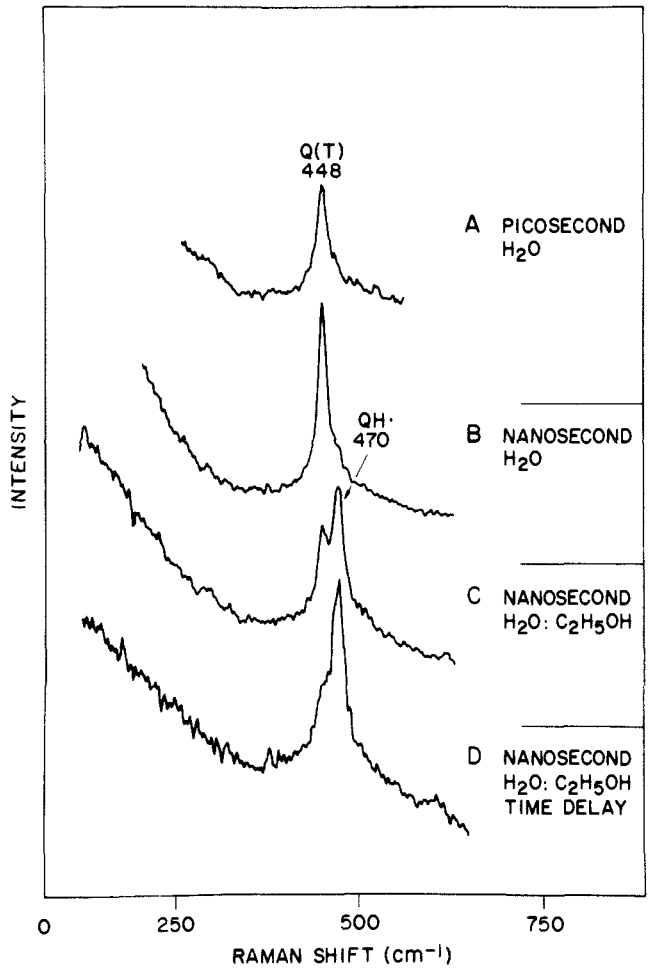

Figure 3. Low-frequency Raman spectra under conditions similar to those of Figure 1. The increasing continuous scattering below 250 cm^{-1} is solvent Raman scattering.

that this line is due to a photoproduct, and we assign it to the 6a ring bending vibration of Q(T). In Figure 3C, a second line appears at 470 cm^{-1} in a solution with 12% ethanol. In Figure 3D the multichannel detector gate is delayed again, and the 470-cm^{-1} line grows at the expense of the Q(T) line. We assign the 470-cm^{-1} line to the 6a vibration of QH·.

Comparison of the data in Figures 1 and 2, taken under identical conditions of fluence and concentration, shows a significant kinetic isotope effect in the abstraction reaction. The QH· lines grow in somewhat more quickly than do the QD· lines. This is common in abstraction reactions.[14]

In contrast, a 5 ± 2 ns delay of the detector gate in the case of trace A in pure water produces no change in the Q(T) spectrum. This result is consistent with the fact that the Q(T) lifetime is ≃200 ns.

In Figures 1A and 2A, there is a small transient peak at 1615 cm^{-1}, labeled ?, at the same position as a strong QH· peak. It does not grow in relative intensity as the detector gate is delayed, and therefore it does not represent QH· coming from reaction with relaxed Q(T). It is either part of the triplet spectrum or represents a small amount of QH· produced during the vibrational relaxation of Q(T).

Traces A and C show the analogous picosecond Raman spectra. In water there is no discernible difference, other than the fractional conversion of S_0 to Q(T). As in the nanosecond spectra, at higher fluences the Q(T) lines increase at the expense of the S_0 line. The fact that the Q(T) spectrum is not shifted or broadened on this time scale is consistent with, but does not rigorously prove, triplet vibrational relaxation being fast on the 20 ps time scale. An analogous observation has been previously made in the picosecond Raman spectra of excited singlet *trans*-stilbene.[5] Additionally, there is no evidence for other transient species preceding relaxed Q(T). Such precursors would be much more prominent in the picosecond data. It is also important to note that, under the conditions of the experiment, there is no evidence for power broadening or stimulated (nonlinear) Raman scattering. The S_0 line remains relatively sharp, and the Q(T) line remains broad as in the nanosecond spectra. These conclusions are also valid in the low-frequency regime for the Q(T) 6a transition observed at ~20 ps in Figure 3B.

The C traces show the observed spectra in the case of water with 10% MeOH solvent. The spectra do *not* show the QH· and QD· present in the corresponding nanosecond spectra, which are virtually identical with the pure water picosecond spectra. These spectra are consistent with the interpretation of the nanosecond spectra: namely, that the QH· and QD· observed appear from relaxed Q(T) reaction with alcohol, with an inverse rate on the order of several nanoseconds. The amount of this reaction in the first 20 ps is experimentally negligible. The spectra also demonstrate that there is no apparent QH· or QD· created during the vibrational relaxation process. In 3:1 H_2O:CH_3OH solvent, the spectra still show only Q(T) without QH:

Discussion

Aqueous Q(T) is present within 20 ps following photon absorption by ground-state *p*-benzoquinone, and its Raman spectrum is fully developed with respect to shape and position. There is no fast semiquinone component, appearing in the 20-ps Raman spectra, either in pure water or in the presence of 10% alcohol. In the presence of 10% alcohol, semiquinone radical appears on the time scale of a few nanoseconds. This result is consistent with quinone preferentially hydrogen bonding to water in the ground state. There must be some diffusion and reorientation before abstraction from a C–H bond takes place. The small peak labeled ? is probably a part of the triplet spectrum.[15] If Q(T) thus has three Raman active a_g fundamentals in the 1600-cm^{-1} region, its symmetry is possibly lower than D_{2h}.[10,12] We conjecture that it might be strongly hydrogen bonded on one end only, with the two carbonyl groups inequivalent in the excited state.

Acknowledgment. We thank E. A. Chandross for useful suggestions concerning an earlier version of this manuscript.

Registry No. H, 12385-13-6; H_2O, 7732-18-5; D_2O, 7789-20-0; CD_3OD, 811-98-3; C_2H_5OH, 64-17-5; CH_3OH, 67-56-1; *p*-benzoquinone, 106-51-4.

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