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LETTERS

Effect of Ionic Modification of the Hydration Shell of a Charge-Neutral Radical on Its Resonance Raman Spectrum

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The effect of ionic perturbation of the hydration shell on the molecular geometry of a charge-neutral radical has been probed by time-resolved resonance Raman spectroscopy using *p*-aminophenoxyl radical ($H_2NC_6H_4O^\bullet$) as a model system. The dynamic coupling between the amine scissors and the ring stretching vibrations is found to be greatly enhanced on incorporation of chloride ion in the hydration shell, suggesting an increase in the coplanar character of the radical. This observed ionic effect, not known previously, contrasts with a recent finding that ions have a negligible effect on the hydrogen-bond structure in liquid water.

Structural studies on the interaction between transient radical intermediates and their chemical environment in liquid water are rare. Infrared studies on a few closed and open-shell ions clustered with water molecules have been performed recently in molecular beam experiments that aim to provide data for modeling the aqueous state.[1] The water molecules that comprise the first hydration shell of a chemical transient in liquid water are generally too few in number to be detected by infrared absorption. Solvent−solute coupling in small size ions in aqueous solution has been examined by resonance Raman spectroscopy[2,3] and, in rare instances when the interaction is fairly strong, the dynamic coupling frequency between the solute radical anion and the hydration shell has been observed.[3] Identification of the solute−solvent coupled mode, without altering the strength of interaction, can be accomplished by replacing light water by heavy water.[3] This interaction can be gradually modified by associating ions with water molecules in the hydration shell. Such an experimental strategy allows examination of the hydration effects even on charge-neutral radicals that may not interact with their aqueous environment as strongly as ions.

In the present study, we have examined the effects of ionic modification of the hydration shell on bond properties of the *p*-aminophenoxyl ($H_2NPhO^\bullet$) radical. This radical has been used as a model system because of the abundance of spectroscopic and structural information available on it in aqueous solution.[4−8] Theoretical studies predict it to be a phenoxyl ($PhO^\bullet$)-like radical in the gas phase.[4,7] However, the physicochemical properties of the radical in water, such as resonance Raman spectra, ESR hyperfine constants, redox potential, and protonation behavior, indicate its structure to be close to that of *p*-benzosemiquinone anion ($PhO_2^{\bullet-}$) and *p*-phenylenediamine cation ($Ph(NH_2)_2^{\bullet+}$) radicals, which have semiquinone characteristics.[6,9] Aqueous $H_2NPhO^\bullet$ can also perform many of the chemical and biological functions of the latter radicals.[10] Although the computed models of $PhO_2^{\bullet-}$ and $Ph(NH_2)_2^{\bullet+}$ provide a reasonable approximation for them in the aqueous state,[11] the gas-phase models of $H_2NPhO^\bullet$ have little correlation with its aqueous state properties.[4,6]

A key feature of the phenoxyl-like structure of $H_2NPhO^\bullet$ is the angle between the ring and the amine plane that in most aromatic amines is close to 45°.[4,9] That the molecular geometry of the radical in water is more nearly planar is inferred from the fact that in its resonance Raman spectrum the NH_2 scissors (bending) mode is appreciably enhanced due to coupling with the planar ring vibration (Wilson mode 8a) of comparable

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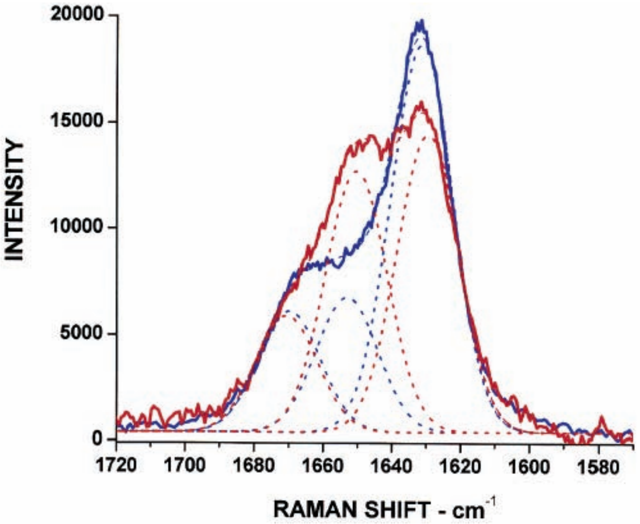

Figure 1. 441 nm Raman spectra of *p*-aminophenoxyl radical ($H_2NPhO^•$) obtained on electron pulse radiolysis of N_2O-saturated aqueous solutions containing 2 mM *p*-aminophenol at pH 11 and 0 M LiCl, (blue) or 8 M LiCl (red). The three components of the observed spectra are indicated in the figure by the dashed Gaussians of the same color. In each case their sum reproduces the experimental spectrum extremely well. Note an increase in the Raman intensity of the 1653 (1650) cm^{-1} band, as compared to the 1670 (1671) and 1632 (1629) cm^{-1} bands, with addition of 8 M LiCl solution.

frequency.[8] If the coupling is caused by the hydrogen-bond interaction between the radical and water molecules, as suggested by the theoretical studies,[4,7] it should be possible to alter its strength by modifying the nature of the hydration shell by ions such as Cl^-. The present study was undertaken to investigate this hypothesis. We find that the presence of ions greatly amplifies the effect of the hydration shell on the mechanical coupling between the NH_2 scissors and the ring stretching vibrations of $H_2NPhO^•$ observed in the 1600−1700 cm^{-1} region.

The *p*-aminophenoxyl radical was prepared in aqueous solution by pulse radiolysis. On electron pulse irradiation of N_2O-saturated water, the $^•OH$ radical is the main reactive species present in solution on the 100 ns time scale.[12] It readily oxidizes *p*-aminophenol ($pK_a = 10.5$) in basic solutions to form *p*-aminophenoxyl radical ($pK_a = 2.2$ for the conjugate acid). In the presence of an excess of LiCl or NaCl in solution, the $^•OH$ radical reacts with Cl^- to form $ClOH^{•-}$ or $Cl_2^{•-}$, which act as secondary oxidants for H_2NPhO^-. Irrespective of the oxidation mechanism, the present studies show that the radical formed is $H_2NPhO^•$. NaCl (0−5 M) and LiCl (0−12 M) were used to modify the structure of the hydration shells of the radical without altering the pH. The pulse radiolysis-time-resolved resonance Raman technique, applied in this study, has been discussed previously elsewhere.[13]

The absorption spectrum of aqueous $H_2NPhO^•$ has a broad peak at 444 (extinction coefficient ∼6.1×10^3 M^{-1} cm^{-1}) and an unresolved shoulder on its lower wavelength side. There is also a very strong absorption peak at 320 nm (extinction coefficient ∼1.5×10^4 M^{-1} cm^{-1}).[4] Raman spectra were generated by excitation at 441 nm.

The 444 nm absorption of the radical has been assigned to a $^2B_1 \rightarrow {}^2B_1$ ($\pi\pi$) transition, with the transition moment along the long molecular axis.[4] Excitation in resonance with this transition enhances only the Franck−Condon modes. Figure 1 displays the Raman spectra in the 1580−1720 cm^{-1} spectral region obtained 1.5 μs after the electron pulse. Background spectra recorded after decay of the radical have been subtracted. The radical decays in the second-order process, with an initial half-period of ∼10 μs ($2k = 1.9 \times 10^9$ M^{-1} s^{-1}), from which the initial radical concentration can be estimated to be about 5×10^{-5} M. The Raman band at 1632 cm^{-1} in Figure 1 is the most intense band in the spectrum. Relatively much weaker bands have been observed at 1432, 1172, 832, and 472 cm^{-1}. These bands have been assigned previously, using purely spectroscopic arguments and by electronic structure computations,[6−8] to the Wilson modes 7a (CO/CN in-phase stretch), 9a (CH bend), 1 (ring breathe), and 6a (ring distortion/CCC bend), respectively. The 1632 cm^{-1} vibration has been assigned to a predominantly ring stretching (Wilson mode 8a) mode.

The band shape in the blue spectrum of Figure 1 is analyzable as the composite of three Gaussian components with centers at 1670, 1653, and 1632 cm^{-1} (blue dashed lines). The bandwidths were taken as ∼18 cm^{-1}. In D_2O solution, where the amine group is deuterated, the 1670 cm^{-1} band shifts downward in frequency to 1659 and the 1632 cm^{-1} band shifts upward to 1639 cm^{-1}. The 1653 cm^{-1} band, associated with the NH_2 scissors mode, on the other hand, disappears from the 1600−1700 cm^{-1} region and appears as the ND_2 scissors at 1178 cm^{-1} with only very low intensity.[4,8] There is no other fundamental expected in the 1600−1700 cm^{-1} region, so that the remaining band at 1670 cm^{-1} in Figure 1 must be assigned to a combination or overtone of a lower frequency mode. It can be readily assigned to the overtone of the ring-breathing mode at 832 cm^{-1}. The ring-breathing frequency shifts to 823 cm^{-1} in D_2O, causing a downward shift in the frequency of its corresponding overtone band to 1659 cm^{-1}.

Resonance Raman spectra were obtained with concentrations of LiCl up to 12 M and NaCl up to 5 M in solution. The spectrum obtained with 8 M LiCl in solution is shown as the red spectrum in Figure 1. From the Gaussian analysis (red dashed lines), a downward shift of about 3 cm^{-1} in the 1632 and 1653 cm^{-1} bands is clearly discernible with the presence in solution of 8 M LiCl. This shift, although very small, is also present in the experiments performed using NaCl. The vibrational frequencies of the other fundamentals in the 400−1800 cm^{-1} region were found to be unaffected, within the experimental error, by addition of salt to the solution.

On addition of salt, the band at 1653 cm^{-1} in water increases in intensity relative to the 1670 and 1632 cm^{-1} bands. It can be readily seen that the intensity of the 1650 cm^{-1} band is almost comparable to that of the 1629 cm^{-1} band. A similar trend was seen on addition of NaCl to the solution. The total intensity of the bands in the 1600−1800 cm^{-1} region, as compared to the rest of the bands in the spectrum, does not appear to change. The 1650 cm^{-1} band acquires more intensity, mostly at the expense of the 1629 cm^{-1} band.

The species responsible for the spectra in Figure 1 is readily attributable to $H_2NPhO^•$, and not to any other transient reaction product, for the following reasons: (1) The Raman spectra in Figure 1 were recorded in resonance with the transient absorption of $H_2NPhO^•$. (2) An increase in the relative intensity of the 1650 cm^{-1} band in the spectrum is the only new feature observed at high salt concentrations. No new bands are seen. (3) The vibrational frequencies do not undergo any significant change on addition of salt. And (4) the 1650 cm^{-1} band decays simultaneously with the 1670 and 1629 cm^{-1} bands, indicating that they represent the same species. It must be concluded that the 1650 cm^{-1} band is enhanced in its relative intensity due to modification of the liquid water structure around the $H_2NPhO^\bullet$ radical.

A high Franck–Condon enhancement of a vibrational mode in the resonance Raman spectra indicates that the excited-state geometry has undergone a large change along the nuclear displacement representing that mode.[14] The 1632 cm^{-1} band is primarily a ring vibration (Wilson mode 8a) in which the central ring CC bonds stretch in phase.[4] Because this band dominates the 441 nm Raman spectra of aqueous $H_2NPhO^\bullet$, it can be safely assumed that the excited-state geometry of the molecule changes along this normal-coordinate; i.e., there is an overall elongation of the ring along the OC- - -CN axis. In view of the $\pi\pi$ nature of the resonant electronic transition, a pure NH_2 scissors motion is unlikely to have a significant effect on the nature of the transition. Therefore, it should not be appreciably resonance enhanced in Raman, unless it couples and borrows intensity from the Wilson 8a ring vibration. We have established previously that this coupling is quite significant.[4] The ND_2 scissors motion, which cannot couple and borrow intensity from the Wilson 8a ring vibration due to mismatch in frequency, is barely observable at 1178 cm^{-1}. This ND_2 vibration is weakly coupled with the moderately enhanced phenyl CH bend (Wilson 9a), which shifts downward to 1164 cm^{-1} on coupling.

Maximum mechanical coupling between the ring and the NH_2 vibrations should occur when they have the same symmetry, their uncoupled frequencies are in close proximity, and the ring and amine groups are coplanar. The coupling between the two vibrations results in two composite modes, one containing a greater contribution from the NH_2 bend (scissors) and the other from the ring stretch (Wilson 8a). In the case of maximum coupling, both vibrational modes would have almost equal contributions from the ring stretch and get equally resonance enhanced in Raman. Therefore, the almost equal intensity of the coupled modes, observed at 1650 and 1629 cm^{-1} in Figure 1 in the presence of 8 M LiCl, is an indication of a geometrical change toward planarity. Also, the ND_2 scissors and phenyl CH bend (Wilson 9a) coupled modes, observed at 1182 and 1159 cm^{-1} in the presence of 8 M LiCl in D_2O solution, appear with nearly equal intensity in resonance Raman due to the enhanced coupling.

It was noted previously that the intensity of a very weak band at 1516 cm^{-1} was indicative of the departure of the radical's π-electronic structure from the D_{2h} symmetry.[4] This band becomes almost unobservable with high salt concentrations in solution, in further support of the conclusion that there is a structural change toward planarity in the presence of high concentrations of Cl^- in solution.

In summary, we have observed a novel hydration effect caused by the introduction of ions in liquid water on the resonance Raman spectra of a charge-neutral, but highly polar, radical. The results reported here are extremely important in view of the recent claim that the hydrogen bonding properties of water molecules are hardly affected by association with ions.[15] Though it is possible that a stronger coupling between the amine scissors and ring stretch vibrations in the presence of ions is caused by other solvent properties, such as dielectric behavior of the medium, microviscosity or intrusion of the radical's amine group into the hydration shell of the Cl^- ion, the vibrational frequencies in benzenoid systems are not very sensitive to the strength of perturbations, internal or external, in contrast to the Raman intensities.[6,16] Therefore, it is not surprising that a change in the orientation of the amine moiety in the radical affects the resonance Raman intensities far more than the vibrational frequencies. The observed phenomenon is important for probing the nature of interaction between a transient solute and its hydration shell by amplifying the strength of interaction by ions.

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