Resonance Raman Spectra of *p*-Benzosemiquinone Anion Dimer

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Resonance Raman specta have been observed for the dimer of *p*-benzosemiquinone anion. When the exciting-light frequency was exactly resonant with the absorption band characteristic of this dimer, a new polarized Raman line appeared at 177 cm^{-1} with a striking resonance enhancement. The resonant behavior and the frequency value both indicate that it can reasonably be assigned to the interradical stretching vibration of the parallel D_{2h} dimer molecule, much as in the case of the previous Würster's cation dimers.

The oxidation-reduction process between quinone and the corresponding hydroxy compound is known to proceed *via* an intermediate radical anion.[1] *p*-Benzosemiquinone anion (SQ^-) can be obtained by oxidizing hydroquinone dissolved in alkaline ethanol with air.[2] The solution is yellow at room temperature due to the absorption bands of SQ^- about 400 nm,[1-5] but it turns blue under −100 °C. The color change is due to the appearance of a new absorption band at 585 nm, as is shown in Fig. 1, which is associated with the formation of an ion dimer $(SQ^-)_2$.[2] The radical anion is also produced by irradiating UV light on a glassy ethanol matrix of hydroquinone at the temperature of liquid N_2.[2,4] The yellow glass thus obtained turns blue when it becomes fluid upon being warmed up to about −130 °C, but the blue color remaining unchanged after it cools down again, indicating the validity of presuming dimer formation.

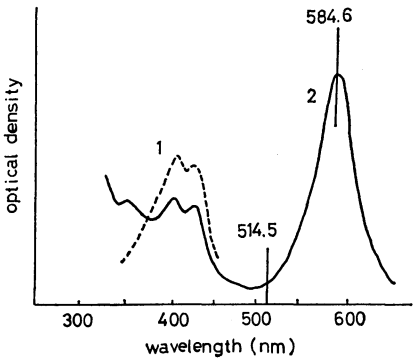

Fig. 1. Electronic absorption spectra of a SQ^- solution at room temperature (Curve 1) and at −196 °C (Curve 2). (from Ref. 2.)

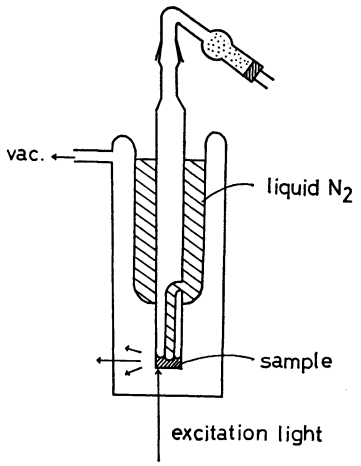

Fig. 2. Raman cell.

The long-wavelength absorption band has assigned to a dimer's transition characterized by interradical charge-transfer, which may affect the interradical binding considerably.[2] Accordingly, there is a good possibility of observing the interradical vibration of $(SQ^-)_2$ in the resonance Raman spectrum associated with the above absorption band, in much the same way as was previously reported for Würster's cation dimers.[6]

Experimental

SQ^- was prepared by oxidizing a 2 mM hydroquinone solution in alkaline ethanol (15 mM KOH) with ambient air. Before the further oxidation to quinone took place, the yellow solution was cooled with liquid N_2 in a proper rate to form a blue glassy matrix in a Raman cell, as is shown in Fig. 2. The Raman spectra were recorded on a JEOL JRS 400D spectrometer, with a CR 52G Ar^+ laser and a CR 590 dye laser (Rhodamine 6G). The dye laser is tuned by bireflingent filters and often brings weak satellite radiations, resulting in spurious lines in the spectra. Therefore, the exciting laser light was passed through a simple dispersing system to eliminate those satellite frequencies.

Results and Discussion

Figure 3 shows the Raman spectra of the blue glassy matrix obtained above by off-resonant 514.5 nm and exactly resonant 584.6 nm exciting radiations. Three Raman lines, at 177, 359, and 545 cm^{-1}, are polarized and are obviously enhanced by the resonance with the 585-nm absorption band. The most strikingly resonant line at 177 cm^{-1} is rather like, in all respects, the interradical vibration of *p*-phenylenediamine cation dimer reported previously,[6] and can probably be assigned to the SQ^--SQ^- stretching mode. We could not obtain a distinct spectrum of the monomer, probably because the resonance enhancement was insufficient to show up the Raman lines in the present dilute solution, but the resonance features of the Raman lines observed above seem to admit no other interpretation than dimer vibrations. The weakly resonant and relatively sharp 359 cm^{-1} and 545 cm^{-1} lines are probably due to such out-of-plane modes of SQ^- moieties that can couple with the interradical stretching, borrowing the intensity from the last mode.

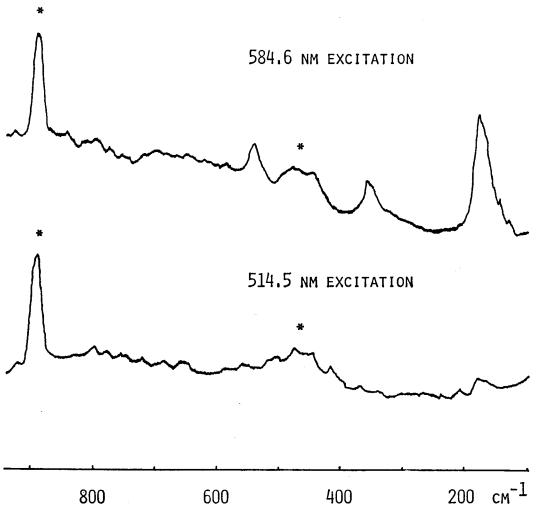

Fig. 3. Raman spectra of $(SQ^-)_2$ in ethanol matrix at −196 °C. * Ethanol lines.

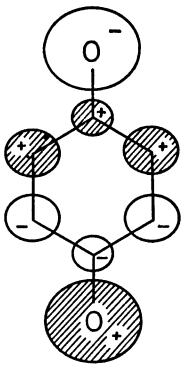

Fig. 4. Illustrated distribution of the b_{3g} molecular orbital of SQ^-.

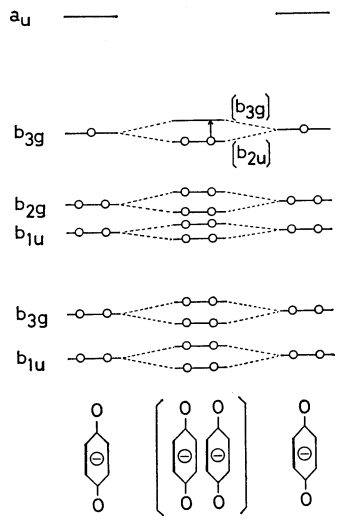

Fig. 5. MO energy scheme for SQ^- and $(SQ^-)_2$.

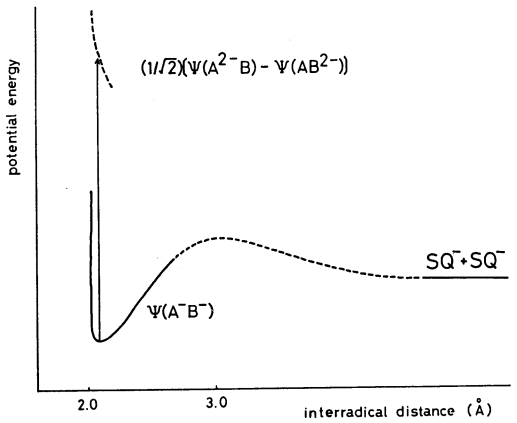

Fig. 6. The potential curve of $(SQ^-)_2$ for changing interradical distance.

The ground state of SQ^- has been shown[7] to be $^2B_{3g}$, principally represented by the π MO configuration:

$$(b_{1u})^2(b_{3g})^2(b_{1u})^2(b_{2g})^2(b_{3g}),$$

where the singly occupied b_{3g} MO has the form illustrated in Fig. 4. Therefore, the formation of the dimer may most reasonably be understood by considering the covalent interaction between the outer b_{3g} MO's for the parallel D_{2h} configuration, as is schematically shown in Fig. 5. The 585 nm absorption is thus assignable to the electron transition $[b_{2u}]\rightarrow[b_{3g}]$, which is characterized by a charge transfer between anion radicals:

$$\Psi(A^-\cdot B^-) \rightarrow (1/\sqrt{2})[\Psi(A^2\text{-}B) - \Psi(AB^{2-})],$$

where A and B represent each SQ monomer. The situation is quite like that of the previous *p*-phenylenediamine cation dimer.[5]

If the 177 cm^{-1} vibration is assumed to be entirely of an interradical stretching mode, the force constant can be calculated to be 1.09 md/Å, very close to the corresponding value of $(PPD^+)_2$.[6] Figure 6 gives the potential curve of $(SQ^-)_2$ for changing the interradical distance, where the part of trapping potential has been calculated by a CNDO approximation† and has been appropriately connected with the level of non-interacting monomer anions calculated on the CNDO basis. The dam in the transitional region is formed by the balance between the long-range electrostatic repulsion and the short-range binding interaction mentioned above. Although the present observed result is inevitably involved in the complex interaction with counter ions and solvent molecules, the binding aspect given above seems essentially applicable.

In conclusion, experimental evidence from vibrational spectroscopy has been given for the dimer formation of *p*-benzosemiquinone anion, indicating a close correspondence to *p*-phenylenediamine cation dimer, in accordance with the theoretical expectation.

References

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† This calculation was carried out on a HITAC 8800/8700 computer system at the Computer Center of the University of Tokyo, using the Y4CB04 library program based on the Q. C. P. E.[8] made by J. A. Pople, D. L. Beveridge, and P. A. Dobosh.

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