Transient Resonance Raman Spectra of 1,5-Dihydroxyanthraquinone in the Lowest Excited Triplet State

Yong Hee Kim, Minjoong Yoon*, Dae Won Cho[t], Sae Chae Jeoung[t], and Dongho Kim[t]

Department of Chemistry, Chungnam National University, Taejon 305-764, Korea
[t]Department of Chemistry, Seonam University, Namwon 590-170, Korea
[t]Spectroscopy Lab. Korea Research Institute of Standards and Science, Taejon 305-606, Korea
Received June 19, 1997

The hydroxyanthraquinones (HAQs) have been considered as chemically important molecules owing to their structural similarity to the quinone antitumor drug[1] as well as the anthraquinoid vat dyes.[2] Among them, 1,5-dihydroxy-anthraquinone (1,5-DHAQ) having an intramolecular hydrogen bonding shows a weak normal fluorescence emission together with a strongly red-shifted emission. The red-shifted emission of 1,5-DHAQ was attributed to the formation of the keto singlet state (K^1) from the enol singlet state (E^1) upon the excited-state intramolecular proton transfer (ESIPT).[3] Such a peculiar property was also seen in 1,8-DHAQ,[4-9] while no evidence of ESIPT has been found for in 1,4-DHAQ and 1-HAQ[10-12] in which the similar intramolecular hydrogen bonding also exists. Most of the earlier studies suggested that the major radiationless decay process of the K^1 state of 1,5-DHAQ is the internal conversion without involving the triplet state. This is based on the fact that no phosphorescence was observed from 1,5-DHAQ. However, Pal et al.[13] observed the short lifetime (*ca.* 3 µs) of the triplet states of 1,5-DHAQ, and they interpreted it to be due to a rapid deactivation of the excited state by reversible hydrogen abstraction reaction across the intramolecular hydrogen bond. Considering this, the triplet state should be also important for the decay process of the K^1 state. Nonetheless little is known about the triplet state of 1,5-DHAQ in connection with the excited-state proton transfer.

It should be emphasized that most spectroscopic studies on the ESIPT in DHAQs have been based on the optical absorption and luminescence techniques which are useful in clarifying the nature of the excited state species and investigating their kinetics. Because the optical spectra measured in solution usually consist of broad bands, it is not easy to get the detailed understanding of the vibrational structure of the photoexcited species. Moreover, there has been much less information on dynamical changes of structure in the triplet excited state with respect to proton transfer. Therefore, in this paper, the transient resonance Raman spectroscopic studies of the lowest excited triplet states of 1,5-DHAQ and deuterated 1,5-DHAQ (1,5-DHAQ-d_2) were carried out in order to gain further insight into the deactivative process and structural features in the excited triplet state.

1,5-DHAQ was purchased from Aldrich Co. and further purified by repeated recrystallization with boiling acetic acid. Deuteration of 1,5-DHAQ was carried out by stirring the sample for 3 hours under dark condition in the methanol-d (CH_3OD from Aldrich Co.; 99.95% isotopic purity) with or without CH_3I; the deuterium substitution of hy-

droxy protons of 1,5-DHAQ almost totally eliminates structure in the absorption spectrum but regularizes the fluorescence profile as previously observed.[4]

The transient resonance Raman system is described in detail in the earlier papers.[14] One-color transient Raman spectra were obtained by employing the intense and weak laser pulse excitation at 435 nm (3.5 ns fwhm at 20 Hz). The pulses at 435 nm were generated from the first anti-Stokes shifted Raman line of H_2 molecules, with the second harmonic pulses from ns Q-switched Nd:YAG laser. The Raman scattering signal was dispersed by a HR 640 spectrograph (Jovin-Yvon) connected with a delay generator (Stanford Research DG 535), a pulse generator (Princeton Instrument FG 135), and a gated intensitified photodiode array detector (Princeton Instrument IRY 700). The sample solutions (*ca.* 1×10^{-4} M) were flowed through a glass capillary (0.8 mm i.d.) with a flow rate sufficient to ensure that each pulse encountered a fresh volume of sample. We carefully checked the sample decomposition by monitoring the ground-state Raman spectra with those of fresh sample, and no evidence of photodecomposition was found.

The absorption maximum of 1,5-DHAQ in CH_3I was observed at 433 nm where the strong (π, π^*) transition was located, and the excited singlet states of the enol form (^1E) can be easily populated by the nanosecond laser pulses at 435 nm. The ^1E state is mostly changed to the ^1K state through the rapid ESIPT with the rate constant greater than 10^{12} s^{-1}.[5,15,16] The ^1K state lifetimes of 1,5-DHAQ in ethanol and that of 1,5-DHAQ-d_2 in CH_3OD were determined to be 330 ps and 1.3 ns, respectively, by measuring the luminescence decay profiles with the time-correlated single photon counting method. These values were in good agreement with the reported values measured in n-hexane (365 ps) and hexane/D_2O (1.2 ns).[5] The deuteration effect on the ^1K state lifetimes has been ascribed to the significant role of the hydrogen-stretching vibrations in radiationless decay process of the ^1K state including internal conversion. However, upon addition of CH_3I to the methanol solution the fluorescence emission was observed to be quite quenched with shortening the ^1K state lifetime (<30 ps). This must be due to the external heavy atom effect resulting in an increase in the intersystem crossing rate to keto triplet (^3K) state. Therefore, we could not detect any Raman spectral features of the singlet state with the nanosecond pulse laser system. In reality the excitation wavelength of 435 nm pulse is in resonance with the T_1-T_n absorption of 1,5-DHAQs, and the intense nanosecond laser pulse at 435 nm populates the excited triplet state of 1,5-DHAQs and simultaneously probes the transient resonance Raman spectrum.
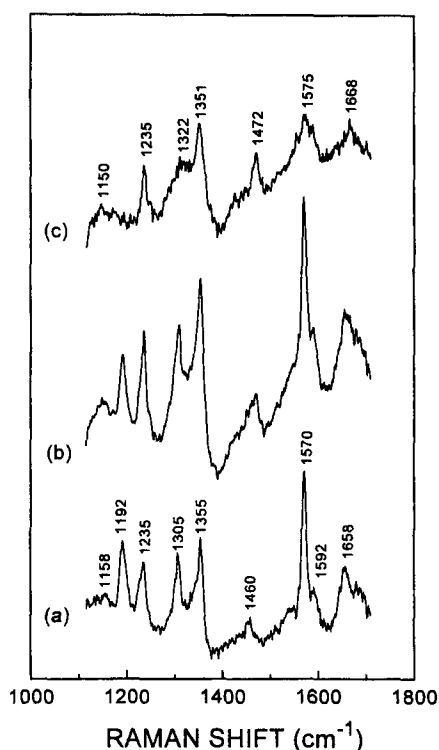
Figure 1. Nanosecond transient resonance Raman spectra of 1,5-DHAQ in CH_3I with 435nm single pulse excitation: (a) lower power (*ca.* 78 J); (b) high power (*ca.* 600 J); (c) difference spectrum (b-a) with a proper subtraction factor.

Figure 1 exhibits the one-color transient resonance Raman spectrum of 1,5-DHAQ in CH_3I. The bottom spectrum was obtained with an excitation of low power pulses at 435 nm. The Raman frequencies are summarized in Table 1. From the comparison with the resonance Raman spectrum of 1-hydroxyanthraquinone (1-HAQ),[17] the 1355 cm^{-1} band was assignable to the C_1-O (and/or C_5-O) stretch of the phenolic moiety. The phenyl ring stretching modes have been assigned to the bands at 1592 (v_1), 1570 (v_2) 1460 (v_3), 1308 (v_4) and 1192 cm^{-1} (v_5), respectively. Especially, the strong 1308 cm^{-1} band is only observed in hydroxy-AQ derivatives,[17] indicating that the ring stretch at 1305 cm^{-1} is coupled with the vibration of the hydroxyl group. The C=O stretching modes were weakly observed at 1658 cm^{-1}. The

Table 1. Frequency of Raman bands of the ground and lowest excited triplet state of 1,5-DHAQs

Assignment	1,5-DHAQ		1,5-DHAQ-d_2	
	S_o	T_1	S_o	T_1
C_9=O (C_{10}=O)	1658	1668 (1322)	1656	1668 (1322)
ring stretching(v_1)	1592		1585	1577
ring stretching(v_2)	1570	1575	1559	1537
ring stretching(v_3)	1460	1472	1450	1453
C_1-O (C_5-O)	1355	1351	1356	1362
ring stretching(v_4)	1305	–	1343	–
OH bending	1235	1235	–	–
ring stretching(v_5)	1192	–	1192	–
CH in-plane bending	1158	1150	1158	1149

lower frequency of the C=O stretch in 1,5-DHAQ compared with that of 9,10-anthraquinone (1665 cm^{-1})[18] is attributable to the enhanced resonating structure through the intramolecular hydrogen bonding with phenolic moiety. The intramolecular hydrogen bonding results in not only lowering C=O bond strength but also enhancing C_1-O bond strength as reflected in the higher frequency of C_1-O compared with that of phenol or 1-HAQ.[17] Unfortunately, we could not observe the O-H stretching mode around 3100 cm^{-1}, since this mode is too weak and overlaps with the fluorescence emission of 1,5-DHAQ. However, the O-H bending mode is observed at 1235 cm^{-1}. The CH in plane bending mode was observed at 1158 cm^{-1}.

The transient resonance Raman spectra of deuterated 1,5-DHAQ-d_2 in a mixture solvent of CH_3I/CH_3OD are shown in Figure 2. The overall spectral features of the ground state Raman spectrum of 1,5-DHAQ-d2 (Figure 2(a)) are similar to those of 1,5-DHAQ. However, as expected, the O-H bending mode (1235 cm^{-1}) of 1,5-DHAQ disappears upon deuteration. This is because the O-D bending mode has lower frequency (*ca.* 980 cm^{-1}) as previously observed for 1-HAQ.[17] It is also interesting to note that the ring stretch of 1,5-DHAQ at 1305 cm^{-1} is shifted to higher frequency at 1343 cm^{-1} upon deuteration of the hydroxyl group. This indicates that the bond strength in the OH-bond-coupled ring of 1,5-DHAQ-d_2 is greater than that of 1,5-DHAQ. This is due to weaker intramolecular hydrogen bonding in 1,5-DHAQ-d_2 compared with that of 1,5-DHAQ. The intramolecular hydrogen-bonding contributes to the enhanced delocalization of electrons in the ring by forming the reso-
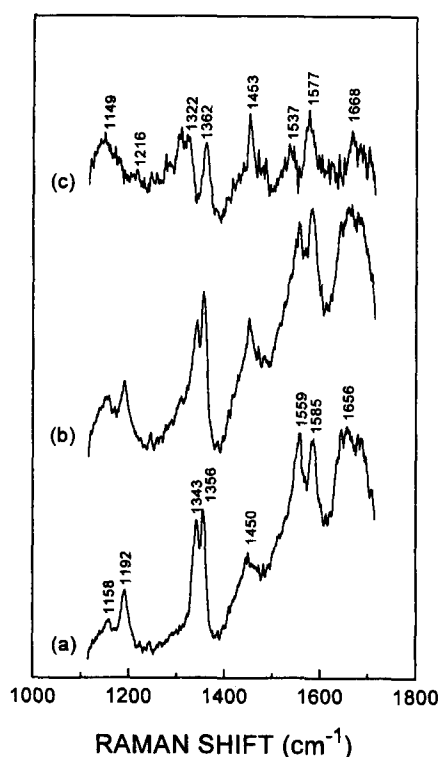

Figure 2. Nanosecond transient resonance Raman spectra of 1,5-DHAQ in CH_3I/CH_3OD(V/V=5:1) with 435 nm single pulse excitation: (a) lower power (*ca.* 78 J); (b) high power (*ca.* 600 J); (c) difference spectrum (b-a) with a proper subtraction factor.

nating structure as described above.

The transient Raman spectra of the excited triplet state were obtained by subtracting the ground state spectral features from high-power spectra with a proper subtraction factor and they are shown in Figures 1(c) and 2(c) for 1,5-DHAQ and its deuterated form, respectively. Assignment of the vibrational modes in the triplet states is also summarized in Table 1. The first characteristic Raman features in the triplet state is the enhancement of the ring streching modes such as v_1, v_2, and v_3. However, the other ring stetches (OH-bond coupled ring stretch (v_4 and v_5)) disappeared in the triplet state. These antiparellel changes in the ring stretches indicate that the π-electronic structure of the ring becomes asymmetric in the triplet state. This is understandable when considering the single proton transfer from 1-OH to $C_9=O$ in the excited state of 1,5-DHAQ in the excited state as proposed in many previous investigations.[16] Actually, the enhancement in the intensity of the O-H bending mode was observed even though the frequency shift is little, indicating that the O-H bond strength decreases upon excitation. Instead, a new band at 1322 cm^{-1} was observed in the excited triplet state. This value is consistent with that obtained previously from the time-resolved Raman spectrum of ^3AQ.[18] Therefore, this band should be originated from the $C_9=O$ (or $C_{10}=O$) stretching mode in the ^3K state. The marked downshift (1656 cm^{-1} in $S_0 \rightarrow$ 1322 cm^{-1} in ^3E) is characteristic of an (n, π^*)-type excited electronic state of a carbonyl compound. This is regarded as a direct indication of the single-bond-like structure of the CO bonding. The marked downshift of the strong $C_9=O$ stretch in the triplet state was also observed for 1,5-DHAQ-d$_2$, exhibiting the aymmetric changes in the ring stretch enhancement. However, one should note that the ring stretches, v_1, and v_2 for 1,5-DHAQ becomes one broadened band in the triplet state while they are just enhanced for 1,5-DHAQ-d$_2$. This may be due to some inhibition of the ESIPT upon deuteration. Thus, these results lead us to conclude that there is the possibility of the aymmetric ESIPT in the triplet state to form the keto form as well as in the singlet state.

References

1. Arcamone, F. *Doxorubicin Anticancer Antibiotics*; Academic Press: New York, 1982.
2. Rembold, M. W.; Karmer, H. E. A. *J. Soc. Dyes Colour.* **1980**, *96, 122.*
3. Standjord, A. S. G.; Barbara, P. F. *J. Phys. Chem.* **1985**, *89*, 2355.
4. Van Benthem, M. H.; Gillispie, G. D. *J. Phys. Chem.* **1984**, *88*, 2954.
5. Flom, S. R.; Barbara, P. F. *J. Phys. Chem.* **1985**, *89*, 4489.
6. Smulevich, G. *J. Chem. Phys.* **1985**, *82*, 14.
7. Smulevich, G.; Foggi, P. *J. Chem. Phys.* **1987**, *87*, 5657.
8. Smulevich, G.; Foggi, P.; Feis, A. and Marzocchi, M. P. *J. Chem. Phys.* **1987**, *87*, 5664.
9. Palit, D. K.; Pal, H.; Mukherjee, T.; Mittal, J. P. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3861.
10. Carter, T. P.; Gillispie, G. D.; Connolly, M. A. *J. Phys. Chem.* **1982**, *86*, 192.
11. Carter, T. P.; Gillispie, G. D.; Connolly, M. A. *J. Phys. Chem.* **1984**, *88*, 2954.
12. Smulevich, G.; Amirav, A.; Even, U.; Jortner, J. *J. Chem. Phys.* **1982**, *73*, 1.
13. Pal, H.; Palit, D. K.; Mukherjee, T.; Mittal, J. P. *J. Photochem. Photobiol. A: Chem.* **1991**, *62*, 183.
14. (a) Jeoung, S. C.; Kim, D.; Cho, D. W.; Yoon, M. *J. Phys. Chem.* **1995**, *99*, 5826. (b) Jeoung, S. C.; Kim, D.; Cho, D. W.; Yoon, M. *J. Phys. Chem.* **1996**, *100*, 3075. (c) Jeoung, S. C.; Kim, D.; Cho, D. W.; Yoon, M. *J. Phys. Chem.* **1996**, *100*, 3075. (d) Jeoung, S. C.; Kim, D.; Cho, D. W.; Yoon, M. *J. Phys. Chem.* **1996**, *100*, 3075.
15. Babara, P. F.; Rentzepis, P. M.; Brus, L. E. *J. Am. Chem. Soc.* **1980**, *102*, 2786.
16. (a) Huston, A.; Scott, G. W.; Gupta, A. *J. Chem. Phys.* **1982**, *76*, 4978. (b) Woessner, G.; Goeller, G.; Kollat, P.; Stezowski, J. J.; Hauser, M.; Klein, U. K.; Kramer, H. E. A. *J. Phys. Chem.* **1984**, *88*, 5544. (c) Flom, S. R.; Babara, P. F. *Chem. Phys. Lett.* **1983**, *94*, 488.
17. Dutta, P. K.; Hutt, J. A. *J. Raman Spectroscs.* **1987**, *18*, 339.
18. VAuthey, E.; Phillips, D.; Parker, A. W. *J. Phys. Chem.* **1992**, *96*, 7356.