Observation of the S_2-Emission from 1,4-Anthraquinone

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Emission, excitation, and absorption spectra of 1,4-anthraquinone (1,4-AQ) have been measured in a degassed CCl_4 fluid solution at different temperatures. It is shown that 1,4-AQ in CCl_4 exhibits weak emission which can be attributed to the $S_2(\pi, \pi^*)$ fluorescence at comparatively high temperature. The $S_2(\pi, \pi^*)$ state is considered to be in thermodynamic equilibrium with the $S_1(n, \pi^*)$ state as well as with the $T_2(n, \pi^*)$ and $T_1(\pi, \pi^*)$ states. The present observation provides the first example of the S_2 emission from the medium-size molecules containing C=O groups.

Recently, assignment and dynamical behavior of the excited states of various types of para quinones have received much attention.[1-6] It is known that some of these molecules exhibit interesting and anomalous emission properties, as are mentioned in detail in a recent review.[4] In order to understand the relationship between the excited-state ordering and the photophysical properties of para quinones, it is of importance to examine the emission properties carefully. It is known that the excited-state ordering of 1,4-anthraquinone (1,4-AQ) is $S_2(\pi, \pi^*) > S_1(n, \pi^*) > T_2(n, \pi^*) > T_1(\pi, \pi^*)$.[4-10] In the systems with such an excited-state ordering, the intersystem crossing, $S_1(n, \pi^*) \rightarrow T_1(\pi, \pi^*)$, is expected to occur predominantly, so that normally the emission observed for such a system is only the phosphorescence from $T_1(\pi, \pi^*)$.[4] In a foregoing paper we have shown that 1,4-AQ in degassed CCl_4 emits the $^1(n, \pi^*)$ fluorescence as a major component of the emission.[11] In the present letter, we show that 1,4-AQ in degassed CCl_4 exhibits weak emission which can be attributed to be originating from the $S_2(\pi, \pi^*)$ state at comparatively high temperatures. The $S_2(\pi, \pi^*)$ state is considered to be in thermodynamic equilibrium with the $S_1(n, \pi^*)$ state, as well as with the $T_2(n, \pi^*)$ and $T_1(\pi, \pi^*)$ states.

1,4-AQ was synthesized and purified in the same way as mentioned in a previous paper.[10] The absence of any impurity emission from a glassy matrix at 77 K and verification that the phosphorescence spectrum in a glassy matrix and the excitation spectrum in CCl_4 agreed well, respectively, with the reported phosphorescence and the corresponding absorption spectra suggested that the purified compound was sufficiently pure for the experiment. The sample solution in a non-fluorescent 10-mm pathlength square quartz cell was degassed carefully by means of repeated freeze-pump-thaw cycles and the sample cell was sealed off on an all-glass vacuum system. The optical density of the sample was always kept below 0.1. Absorption spectra were measured with a Hitachi 220A or a Hitachi 200-10 spectrophotometer and the emission and excitation spectra were measured with a Spex Fluorolog-2/model 211-340, a Hitachi F-400 or a Hitachi 650-10S fluorescence spectrophotometer.

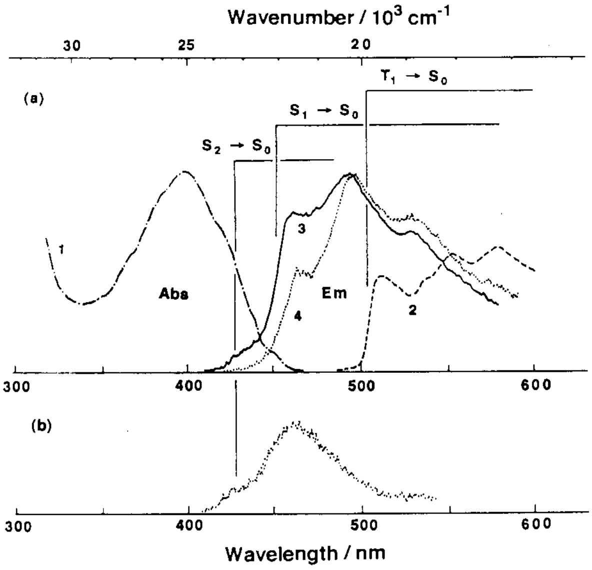

Figure 1. (**a**) Absorption spectrum at room temperature (1), the phosphorescence spectrum at 77 K (2), and emission spectra at two different temperatures (3 and 4) for 1,4-AQ in CCl_4: (3) 55 °C; (4) 0 °C. The emission spectra 3 and 4 are normalized to a common magnitude. (**b**) The difference spectrum obtained by subtracting the emission profile at 55 °C from that at 0 °C for 1,4-AQ in CCl_4.

Figure 1(a) shows the emission spectra at different temperatures, together with the absorption spectrum of 1,4-AQ in CCl_4 at room temperature. A weak absorption band on the shoulder of the $S_0 \rightarrow S_2(\pi, \pi^*)$ absorption spectrum is due to the transition to the $S_1(n, \pi^*)$ state which obtain the intensity mainly through the vibronic coupling with the upper $^1(\pi, \pi^*)$ states.[4,5] In non-polar hydrocarbons this weak band is observed clearly at the red side of the $S_0 \rightarrow S_2(\pi, \pi^*)$ absorption band, but in CCl_4 this band is observed merely as a shoulder at the onset of the $S_2(\pi, \pi^*)$ absorption. The emission at 77 K is safely attributed to the $T_1(\pi, \pi^*)$ phosphorescence. It has already shown that the emission of 1,4-AQ in CCl_4 at temperatures near room temperature consists of the fluorescence from $S_1(n, \pi^*)$ which is in thermodynamic equilibrium with $T_1(\pi, \pi^*)$. Closer inspection of the emission spectra reveals that there is a shoulder in the short-wavelength tail of the S_1 fluorescence, the relative intensity of which increases with elevation of the temperature. The difference spectrum obtained by subtracting the emission profile at lower temperature from that at higher temperature, after multiplying an appropriate constant to the latter, is shown in Figure 1(b) for 1,4-AQ in CCl_4. The profile of the difference spectrum is centered at around 460 nm, which is significantly shifted to the blue from the emission center of the S_1 fluorescence (~500 nm).

The emission observed at short-wavelength tail of the S_1 fluorescence of 1,4-AQ in a degassed CCl_4 fluid solution is assigned to the fluorescence from the $S_2(\pi, \pi^*)$ state which is in thermodynamic equilibrium with $S_1(n, \pi^*)$ as well as with $T_2(n, \pi^*)$ and $T_1(n, \pi^*)$. This assignment is based on the following observations: (1) The emission spectrum shows the expected mirror-image relationship to the $S_0 \rightarrow S_2(\pi, \pi^*)$ absorption spectrum, not to the $S_0 \rightarrow S_1(\pi, \pi^*)$ spectrum, with a sufficient overlapping between the emission and absorption spectra; (2) the corrected excitation spectrum and the absorption spectrum are identical in the range 280–400 nm; and (3) the emission intensity of the S_2 emission relative to the S_1 fluorescence increases with increasing temperature.

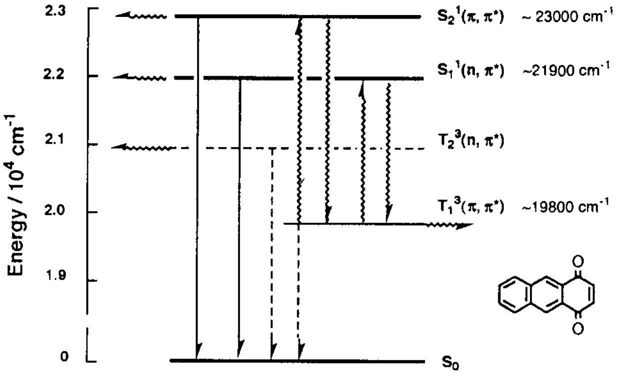

Figure 2. An energy level scheme including the relaxation processes for 1,4-AQ in CCl_4.

The energy diagram for 1,4-AQ in CCl_4 including the relaxation processes is presented in Figure 2. The spectroscopically estimated energy separation between $S_1(n, \pi^*)$ and $S_2(\pi, \pi^*)$, ΔE, is about 1000 cm^{-1}. When two closely-located electronic states are in thermodynamic equilibrium, the quantum yield ratio of the emission from the upper state (S_2) to that from the lower state (S_1) is proportional to the value, $\exp(-\Delta E/kT)$. Hence, the quantum yield ratio, Φ_{F_2}/Φ_{F_1}, is expressed approximately by [4]

$$\Phi_{F_2}/\Phi_{F_1} = k_{F_2}\exp[-\Delta E/kT]/k_{F_1}, \qquad (1)$$

where k is the Boltzmann constant, T is the absolute temperature and k_{F_2} and k_{F_1} are, respectively, the radiative rate constants of S_2 and S_1. Occurrence of the S_2 fluorescence from 1,4-AQ is not surprising so far as the temperatures used in the present study are concerned. According to Eq (1) the quantum yield ratio Φ_{F_2}/Φ_{F_1} is estimated to be 0.7 at 330 K for ΔE = 1100 cm^{-1} and k_{F_2}/k_{F_1} ~ 80. Thus, the observed spectrum is to a good approximation just the superposition of the S_1 and S_2 fluorescence.

In conclusion, the emission of 1,4-AQ observed in a carefully degassed CCl_4 fluid solution at comparatively high temperature (50–70 °C) consists of $S_1(n, \pi^*)$ fluorescence accompanied by weak $S_2(\pi, \pi^*)$ fluorescence. Temperature dependence of the emission spectrum indicates that the S_2 and S_1 states are in thermodynamic equilibrium. The present observation provides the first example of the S_2 emission from the medium-size molecules containing C=O groups and may contribute to the development of the photochemical processes utilizing the higher excited state. Occurrence of the S_2 and S_1 emission is related to the electronic structure of 1,4-AQ, in which both the S_1 - S_2 (~1100 cm^{-1}) and S_1 - T_1 energy separations (~2000 cm^{-1}) are comparatively small.

References and Notes

1 R. S. Becker and L. V. Natarajan, *J. Phys. Chem.*, **97**, 344 (1993).

2 A. N. Diaz, *J. Photochem. Photobiol. A* , **53**, 141 (1990).

3 I. Amada, M. Yamaji, M. Sase, and H. Shizuka, *J. Chem. Soc., Faraday Trans.*, **91**, 2751 (1995).

4 T. Itoh, *Chem. Rev.*, **95**, 2351 (1995), and references cited therein.

5 T. Itoh, *Spectrosc. Lett.*, **29**, 417 (1996).

6 T. Yoshihara, M. Yamaji, T. Itoh, H. Shizuka, T. Shimokage, and S. Tero-Kubota, *Phys. Chem. Chem. Phys.*, **2**, 993 (2000).

7 M. Zander, *Ber. Bunsen-Ges. Phys. Chem.*, **71**, 424 (1967).

8 M. Nepras and A. Novak, *Collect. Czech. Chem. Commun.*, **42**, 2343 (1977).

9 A. Novak, M. Titz and M. Nepras, *Collect. Czech. Chem. Commun.*, **39**, 1532 (1974).

10 G. Olbrich, O. E. Polansky, and M. Zander, *Ber. Bunsen-Ges. Phys. Chem.*, **81**, 629 (1977).

11 T. Itoh, M. Yamaji, and H. Shizuka, *Chem. Phys. Lett.*, **273**, 397 (1997).