Emission Spectra of 1,4-Naphthoquinone and Its 2-Methyl Derivative in the Vapor Phase

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The emission spectra of 1,4-naphthoquinone (NQ) and 2-methyl-1,4-naphthoquinone (MNQ) vapors have been investigated at various temperatures in the presence of added foreign gases (≈100 Torr). The results indicate that in both NQ and MNQ the emission consists of $T_1(n, \pi^*) \rightarrow S_0$ phosphorescence and weak E-type delayed fluorescence, $S_1(n, \pi^*) \rightarrow S_0$, the latter lying at higher frequencies. This new interpretation of the vapor-phase emission spectra of the naphthoquinones, which is substantially different from the interpretations given by previous authors, is based on and consistent with the following observations: (1) When the temperature is raised, the ratio of the fluorescence intensity to the phosphorescence intensity increases; (2) the S_1—T_1 energy separations, 1365±60 and 1500±200 cm^{-1} for NQ and MNQ, respectively, determined from the temperature dependence of the emission intensities agree with the corresponding values obtained from spectral data; (3) the emission lifetimes obtained by monitoring the fluorescence and phosphorescence are identical.

1,4-Naphthoquinone (NQ) is one of the representative quinones and shows strong emission in the visible region in rigid glass solution at 77 K. This emission has been identified as the phosphorescence from the lowest triplet state of n, π^* type, on the basis of the prominent progression in the C–O stretching vibration, the short lifetime, and the band position.[1] A comparison of the phosphorescence and absorption spectra of NQ indicates that the energy difference between the lowest excited singlet and triplet states is very small.

It is known that NQ exhibits weak emission in the vapor phase, and studies have been made on both emission[2,3] and absorption spectra[4] of NQ vapor. The vapor-phase emission spectrum of NQ was obtained in the presence of added benzene by Singh and Singh[2] and by Longin[3] with the aid of discharge excitation, but their assignments of the emitting states are inconsistent with each other. The former authors interpreted the emission spectrum in terms of fluorescence from a $^1(n, \pi^*)$ state and phosphorescence from a $^3(n, \pi^*)$ state, with the origins at 21945 and 18782 cm^{-1}, respectively, while the latter regarded the spectrum as due to two kinds of fluorescence from different n, π^* states with the origins at 22163 and 21974 cm^{-1}.

The emission and absorption spectra of 2-methyl-1,4-naphthoquinone (MNQ) vapor also were reported by Baruah *et al.*[5] They interpreted the emission as consisting of fluorescence from a $^1(n, \pi^*)$ state and phosphorescence from a $^3(n, \pi^*)$ state, with origins at 22075 and 20262 cm^{-1}, respectively.

Since the phosphorescent carbonyl compounds having a small S_1-T_1 energy separation often show weak E-type delayed fluorescence at room temperature,[6] one must take this into account in the assignment of the emitting states of NQ or MNQ vapor.

The purpose of the present study is to clarify the emitting states of NQ and MNQ in the vapor phase. Particular attention has been directed to the change of emission spectra with temperature. It is shown that, at high total pressure (≈100 Torr) in the presence of a foreign gas, the emission spectra of NQ and MNQ vapors consist of $T_1(n, \pi^*) \rightarrow S_0$ phosphorescence and weak E-type delayed fluorescence, $S_1(n, \pi^*) \rightarrow S_0$. The S_1-T_1 energy gaps obtained from the temperature dependence of emission spectra are in agreement with those obtained from the band positions. The results of the decay measurement also support the present assignment.

Experimental

Materials. 1,4-Naphthoquinone (NQ), obtained from Wako Pure Chemical Industries, was recrystallized several times from ethanol, passed through a silica-gel column with benzene or petroleum benzine as the solvent, and finally sublimed *in vacuo*. 2-Methyl-1,4-naphthoquinone (MNQ) from Tokyo Chemical Industries was recrystallized several times from ethanol and sublimed *in vacuo*. It was confirmed that the emission spectra of these purified materials in a rigid glass at 77 K agree well with those reported previously.[1,7] Carbon tetrachloride of spectroscopic quality from Merck and benzene of chromatographic quality from Nakarai Chemicals were used as foreign gases without further purification.

Apparatus and Procedure. Emission and excitation spectra were measured with a high-sensitivity spectrophotometer based on the photon-counting method; it is equipped with a xenon lamp and a double monochromator for excitation, and with an HTV R-585 photomultiplier.[8] Two reflecting concave mirrors were placed beside the sample cell so as to intensify the emission signal. Absorption spectra were obtained with a Hitachi EPS-3 or a Cary-15 spectrophotometer. Emission decays were measured with a spectrophosphorimeter which was specially designed for measuring lifetimes ranging from 10^{-2} to 10^{-5} s by means of the photon-counting method.[9] Quartz cells of 35-mm path length were used for measuring emission and excitation spectra as well as emission decays. Samples were degassed in a mercury-free vacuum system.

Emission spectra were corrected for the spectral sensitivity of the monochromator-photomultiplier system with a solution of quinine in 0.5 M sulfuric acid as a standard. Excitation spectra were corrected for the spectral intensity distribution of the exciting light by the use of an aqueous solution of rhodamine B as a quantum counter. Emission quantum yields were determined by comparing the corrected emission spectra of the sample vapors with that of quinine in 0.5 M sulfuric acid, which is known to have an emission quantum yield of 0.51.[10]

Results

Figure 1 shows the corrected emission spectra in

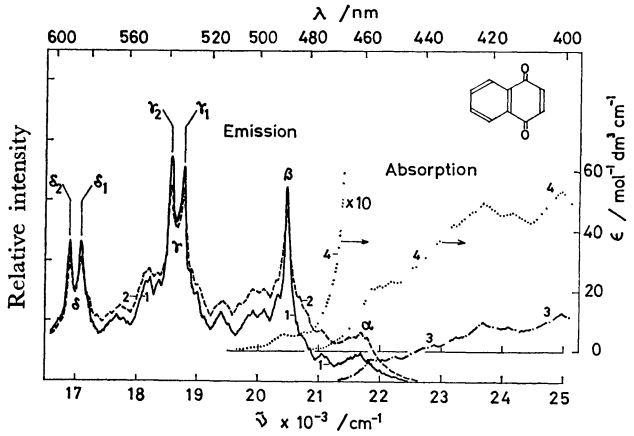

Fig. 1. Vapor-phase emission spectra (corrected) in the presence of benzene vapor (≈100 Torr) at different temperatures (1 and 2) and absorption spectra (3 and 4) of 1,4-naphthoquinone: (1) at 15 °C; (2) at 85 °C; (3) in the vapor phase; (4) in isopentane solution at room temperature. The intensity of spectrum 2 is arbitrarily chosen with no relation to that of spectrum 1. Emission spectra were obtained with a bandwidth of 1.0 nm.

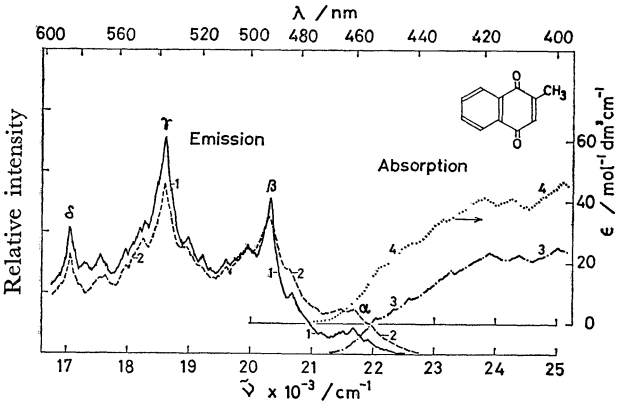

Fig. 2. Vapor-phase emission spectra (corrected) in the presence of benzene vapor (≈100 Torr) at different temperatures (1 and 2), vapor-phase excitation spectrum (3), and absorption spectrum in isopentane at room temperature (4) of 2-methyl-1,4-naphthoquinone: (1) at 25 °C; (2) at 80 °C. The intensity of spectrum 2 is arbitrarily chosen with no relation to that of spectrum 1. Emission spectra were obtained with a bandwidth of 2.0 nm.

the presence of benzene (≈100 Torr) at two temperatures and the absorption spectrum of NQ vapor, where the main emission bands are denoted by α, β, γ, and δ. Bands γ and δ split into doublets, *i.e.* γ_1 and γ_2, and δ_1 and δ_2, respectively. When the temperature is raised, the ratio of the intensity of band α to that of band β, γ, or δ increases. Band α has a sort of mirror-image relation to the vapor-phase absorption spectrum. Band β agrees in position with the very weak band which appears at about 20500 cm^{-1} in the absorption spectrum in isopentane solution (Fig. 1). This weak absorption band can be attributed to $S_0 \rightarrow T_1(n, \pi^*)$ transition on account of its small molar extinction coefficient ($\varepsilon \simeq 0.4$ mol^{-1} dm^3 cm^{-1}). The excitation spectra monitored at bands α, β, γ_1, and γ_2 agree well with the absorption spectrum. The absorption spectrum of NQ vapor ranging from 2.1 to 2.8×10^4 cm^{-1} can safely be assigned as the $S_0 \rightarrow S_1(n, \pi^*)$ transition on the basis of the molar extinction coefficients for the corresponding absorption in isopentane, although Singh and Singh[4] regarded it as consisting of transitions from the ground state to a $^1(n, \pi^*)$ state and a $^3(n, \pi^*)$ state with the origins at 23161 and 21944 cm^{-1}, respectively.

Figure 2 shows the corrected emission spectra of MNQ vapor in the presence of benzene (≈100 Torr) at two temperatures, the vapor-phase excitation spectrum, and the absorption spectrum in isopentane solution. As is seen in Fig. 2, the intensity distribution of the emission spectrum changes with temperature in much the same way as that of NQ vapor. Band α for MNQ vapor also has a sort of mirror-image relation to the vapor-phase excitation spectrum and to the absorption in isopentane solution in the $S_0 \rightarrow S_1(n, \pi^*)$ region. The absorption spectrum of MNQ vapor in the $S_0 \rightarrow S_1$ region could not be obtained. It is assumed that the vapor-phase excitation spectrum, which resembles the absorption spectrum in isopentane, can be used as a substitute for the vapor-phase absorption spectrum. The excitation spectrum of MNQ vapor in the $S_0 \rightarrow S_2(\pi, \pi^*)$ region (2.8—3.6×10^4 cm^{-1}) was found to agree well with the corresponding vapor-phase absorption spectrum. The emission spectra of NQ and MNQ vapors obtained in the present study are somewhat different in structure from the previous results.[2,3,5]

In the present experiment, carbon tetrachloride as well as benzene was used as a foreign gas. These compounds have the same effect on NQ and MNQ vapors with respect to the temperature dependence of the emission spectra and to the relation between excitation and absorption spectra. Both benzene and carbon tetrachloride are considered to induce collisional deactivation of excited vibronic levels of NQ and MNQ vapor. Benzene, however, has an additional effect: When NQ (or MNQ) vapor is excited in the presence of benzene at wavelengths where benzene absorbs (<260 nm), intense emission is observed. The spectrum of this emission is identical with the emission spectrum of NQ (or MNQ), but the excitation spectrum for the emission agrees with the absorption spectrum of benzene vapor. On reference to the electronic energy levels of NQ (or MNQ) and benzene, one is led to the conclusion that actually the emission in question occurs through energy transfer from benzene to NQ (or MNQ). We thus utilized benzene not only as an inert foreign gas but also as an energy donor in order to obtain strong emission from NQ (or MNQ).

Figure 3 shows the emission spectra of NQ and MNQ in rigid glass solution at 77 K. Except for the absence of band α, these spectra resemble the corresponding vapor-phase emission spectra. With NQ in the rigid glass solution, however, the second and third bands, which belong to the prominent progression in the C–O stretching vibration, do not show such doublets as observed in the case of the vapor-phase emission spectrum (bands γ_1 and γ_2, and δ_1 and δ_2 in Fig. 1).

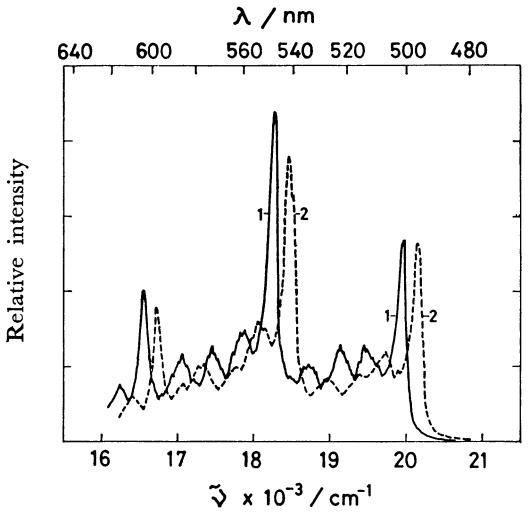

Fig. 3. Emission spectra (corrected) of 1,4-naphthoquinone (1) and 2-methyl-1,4-naphthoquinone (2) in an isopentane-methylcyclohexane (1:1) mixture at 77 K.

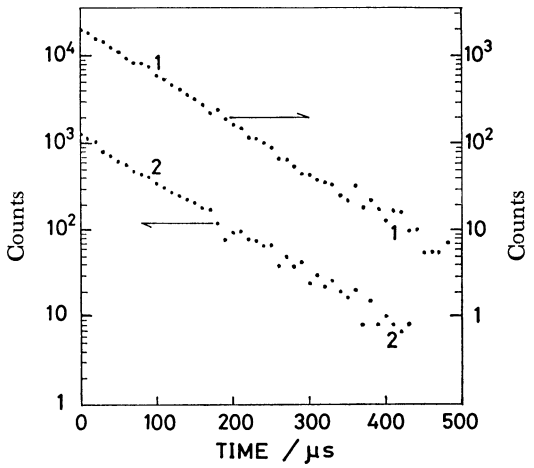

Fig. 4. Typical semilogarithmic plots of emission intensity vs. time for 1,4-naphthoquinone vapor in the presence of added CCl_4 ($\approx$100 Torr) at 80 °C: (1) monitored at band α; (2) at band β. Emission decays were obtained with a bandwidth of 20 nm for the detection monochromator.

Emission decays of NQ vapor in the presence of carbon tetrachloride ($\approx$100 Torr) are shown in Fig. 4. The lifetimes monitored at bands α, β, and γ_1 were found to be the same (84 μs) and independent of the excitation energy. The decay of the emission of MNQ vapor could not be measured because of its low quantum yield. The emission quantum yields were determined to be 1.5×10^{-2} for NQ and 9.5×10^{-4} for MNQ vapor at 80 °C in the presence of carbon tetrachloride.

Discussion

The vapor-phase emission spectra of NQ and MNQ obtained in the present study show characteristic temperature dependence; that is, the ratios of the intensity of band α to those of the other bands increase, when

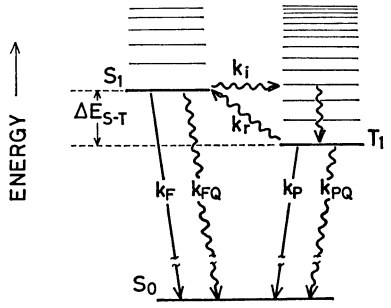

Fig. 5. Kinetic scheme and the rate constants for the radiative (→) and nonradiative (⇝) processes of naphthoquinone vapors in the presence of an added foreign gas.

the temperature is raised. We assign band α to the $S_1(n, \pi^*)\rightarrow S_0$ fluorescence and bands β, γ, and δ to the $T_1(n, \pi^*)\rightarrow S_0$ phosphorescence. This assignment is based on the mirror-image relation between vapor-phase emission and absorption spectra and on the similarity between the emission spectrum in the vapor and the phosphorescence spectrum in the rigid glass. For both NQ and MNQ vapors (Figs. 1 and 2), band β can be taken as the origin of the phosphorescence; and the peak on the higher-wavenumber side of band α is taken as the fluorescence origin, since it coincides in position with a peak that appears in the vapor-phase absorption or excitation spectrum. Thus, the origins of phosphorescence are located at 20460 and 20340 cm^{-1}, and those of fluorescence at 21830 and 21950 cm^{-1}, respectively, for NQ and MNQ vapors. The S_1-T_1 energy separations, ΔE_{S-T}, are thus found to be 1370 cm^{-1} for NQ and 1610 cm^{-1} for MNQ vapor. It then follows from Figs. 1 and 2 that the ratio of the fluorescence intensity to the phosphorescence intensity increases with temperature. In view of this observation, we assign the fluorescence of the naphthoquinone vapors to E-type delayed fluorescence.

The kinetic scheme for the electronic relaxation processes in the naphthoquinone vapors, including E-type delayed fluorescence, is illustrated in Fig. 5 together with various rate constants: k_F and k_P are the radiative rate constants, and k_{FQ} and k_{PQ} are the nonradiative rate constants, respectively, from S_1 and T_1 to the ground state, S_0; k_i represents the rate constant for the intersystem crossing; k_r is the rate constant for thermal activation to upper vibrational levels of T_1 followed by reverse intersystem crossing to S_1, and it can be written in the form[11]

$$k_r = k_r^0 \exp\left(\frac{-\Delta E_{S-T}}{kT}\right), \quad (1)$$

where k and T are the Boltzmann constant and absolute temperature, respectively, and k_r^0 represents a temperature-independent term.

According to the kinetic scheme, the ratio of the quantum yield of the delayed fluorescence, Φ_{DF}, to that of phosphorescence, Φ_P, is given by

$$\frac{\Phi_{DF}}{\Phi_P} = \frac{k_F k_r^0}{k_P(k_F+k_{FQ}+k_i)} \exp\left(\frac{-\Delta E_{S-T}}{kT}\right). \quad (2)$$

Therefore, ΔE_{S-T} can be derived from the variation

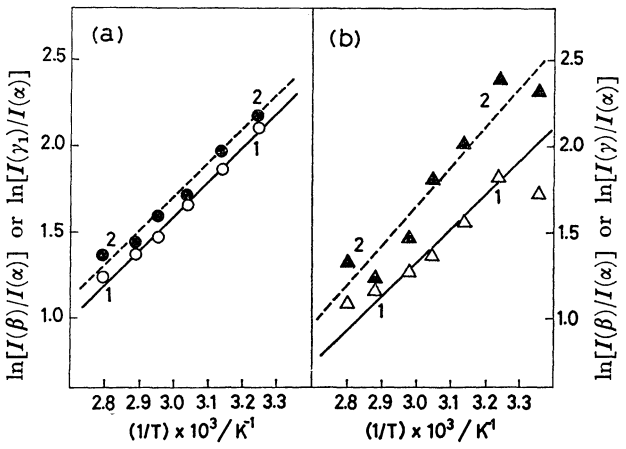

Fig. 6. Temperature dependence of ratios between band intensities for (a) 1,4-naphthoquinone and (b) 2-methyl-1,4-naphthoquinone vapors: (1) $\ln[I(\beta)/I(\alpha)]$ *vs.* $1/T$; (2) $\ln[I(\gamma_1)/I(\alpha)]$ or $\ln[I(\gamma)/I(\alpha)]$ *vs.* $1/T$. Essentially the same results were obtained by using benzene and carbon tetrachloride as foreign gases.

of Φ_{DF}/Φ_P with T. We use peak-intensity ratios instead of the quantum-yield ratios; the peak intensities of bands α, β, and γ will be denoted by $I(\alpha)$, $I(\beta)$, and $I(\gamma)$, respectively.

Figure 6 shows the plots of $\ln[I(\beta)/I(\alpha)]$ and $\ln[I(\gamma)/I(\alpha)]$ against $1/T$ for NQ and MNQ vapors. In the case of NQ, the peak intensity of band γ_1 is used instead of $I(\gamma)$. The plots give straight lines, and the values of ΔE_{S-T} calculated from the slopes are 1365±60 and 1500±200 cm^{-1} for NQ and MNQ vapors, respectively. These values agree well with the spectroscopically estimated gaps of 1370 cm^{-1} for NQ and 1610 cm^{-1} for MNQ, thus confirming the occurrence of E-type delayed fluorescence. Since the intensities of the emission bands other than band α change in the same way when the temperature is changed, the main emission bands located at wavenumbers lower than about 2.1×10^4 cm^{-1} can be regarded as due to a single electronic transition, $T_1\rightarrow S_0$, for both NQ and MNQ vapors.

The fact that the lifetimes of NQ vapor monitored at bands α and β are the same also supports our interpretation of the emission spectra, because according to the kinetic scheme in Fig. 5 the concentration of the S_1 molecule is to be proportional to that of the T_1 molecule. It is certain that the T_1 state is of an n, π^* type on account of its relatively short lifetime.

Our assignment for NQ vapor differs entirely from the ones presented by the previous authors. There are marked differences between the present and previous assignments also for MNQ vapor. The previous authors[5] assigned a relatively weak band of MNQ at 20262 cm^{-1} to the origin of phosphorescence and some of very strong bands at wavenumbers lower than 2.1×10^4 cm^{-1} to fluorescence. Moreover, none was pointed out as to the mechanism of the occurrence of fluorescence emission. Although our spectral measurement was performed with lower resolution, the temperature dependence of the emission spectra along with the results of the lifetime measurement indubitably indicates that the emission spectra of NQ and MNQ vapors at high total pressures consist of phosphorescence and E-type delayed fluorescence.

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