Bull. Chem. Soc. Jpn., **69**, 2191—2194 (1996)

Analysis of the Excitation and Emission Spectra of Tungstates and Molybdate

Nobuhiro Saito, Noriyuki Sonoyama, and Tadayoshi Sakata*

Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering,
Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226

(Received March 13, 1996)

The excitation and emission spectra of $CaWO_4$, $MgWO_4$, $PbWO_4$, $ZnWO_4$, and $CaMoO_4$ were analyzed by a configurational coordination model. The spectral line shapes simulated by a configurational coordination model with a singlet ground state and an excited triplet state well explained the line shape of the luminescence spectra and the line shape at the rising part of the excitation spectra of these salts at room temperature. The energy level of the excited triplet state and the reorganization energies at the ground sate and the triplet state were determined. It was concluded that the potential curve at the excited state becomes shallower than that at the ground state for these systems.

Tungstates represented by $CaWO_4$ and molybdates represented by $CaMoO_4$ are known to be pure phosphors, which show luminescence without any activators. Those calcium salts are widely used as phosphors. The emission center of tungstates and molybdates is $WO_4{}^{2-}$ and $MoO_4{}^{2-}$, respectively. The excitation and emission of these ions have been assigned to the transition between $5d^0$ at W^{6+} (or $4d^0$ at Mo^{6+}) and $2p^6$ at O^{2-}.[1—5] The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the tungstates and molybdates are $1t_1$ and 2e, respectively.[1,5—7] Taking into consideration the spin multiplicity and T_d symmetry of $WO_4{}^{2-}$ and $MoO_4{}^{2-}$, $WO_4{}^{2-}$, and $MoO_4{}^{2-}$ have four excited states ($^1T_2$, $^3T_2$, $^1T_1$, and $^3T_1$). Among the transitions between the excited states and the $^1A_1$ ground state, only the transition between $^1A_1$ and $^1T_2$ is optically allowed. A molecular orbital calculation determined the order of the energy levels of the excited states: $^3T_1 \leqq {}^3T_2 < {}^1T_1 < {}^1T_2$.[1,5,7] The emission of the tungstates and molybdates has been assigned to a transition from triplet $^3T_1$ to the ground state, $^1A_1$. Normally, this transition is spin forbidden. However, in the case of the tungstates and molybdates, a spin-orbit coupling[1,2,5] or phonon coupling[6] is thought to make this transition allowed. In a previous study we developed a synthetic method for producing transparent thin films of tungstates.[8] On the basis of the absorption spectra of the thin films synthesized by this method, we assigned the excitation of the tungstates around 2.5 eV to the transition from the ground state ($^1A_1$) to the triplet charge-transfer excited state ($^3T_1$). In the present work, we analyzed the emission and excitation spectra of tungstate and molybdate thin films using a configurational coordination model of a singlet ground state-triplet excited state.

Experimental

$CaWO_4$, $MgWO_4$, $PbWO_4$, and $ZnWO_4$ thin films were prepared by the heat reaction of metal-oxide thin films with WO_3 vapor.[8] A $CaMoO_4$ thin film was prepared by the heat reaction of a CaO thin film with MoO_3 vapor at 800 °C for 10 h. The thickness of these films were 0.1—1 μm. The excitation and emission spectra were measured using a spectrofluorometer (SPEX, Fluoromax [(TM)]) in air at room-temperature. The excitation light power was corrected using a radiometer (Eppley Laboratory, 21666). The photomultiplier-tube sensitivity was not corrected.

Results and Discussion

The solid lines in Figs. 1, 2, and 3 show the photoluminescence and excitation spectra of several tungstates and calcium molybdate at room temperature. Here, we assume that the excitation and luminescence of those tungstates and molybdate are based on the $^1A_1$–$^3T_1$ transition. It is also assumed that the potential curves of the $^1A_1$ and $^3T_1$ states are represented by the quadratic functions $E_G(x)$ and $E^*(x)$, as shown in Fig. 4. In Fig. 4, E_0 represents the energy level

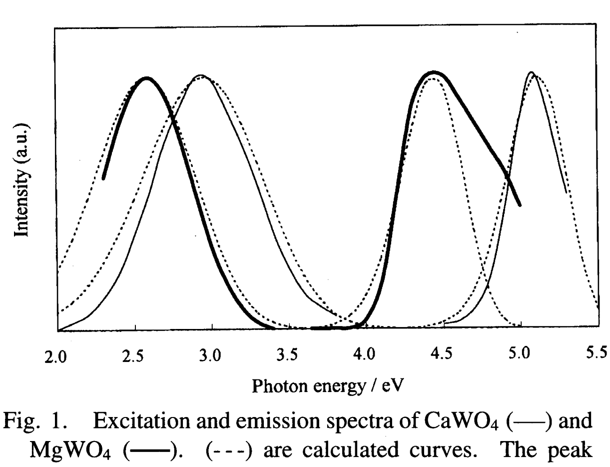

Fig. 1. Excitation and emission spectra of $CaWO_4$ (—) and $MgWO_4$ (——). (- - -) are calculated curves. The peak positions in the excitation and emission spectra were used for the emission and excitation measurement, respectively.

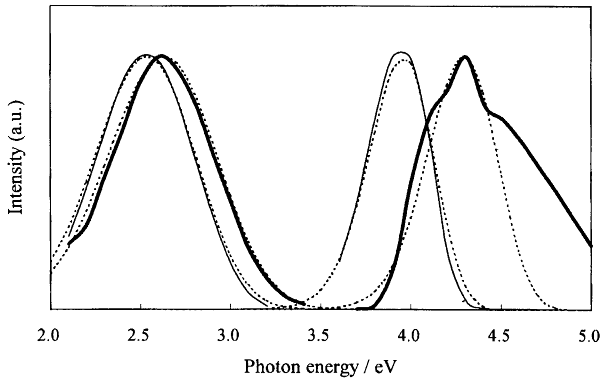

Fig. 2. Excitation and emission spectra of $PbWO_4$ (—) and $ZnWO_4$ (——). (- - -) are calculated curves. The peak positions in the excitation and emission spectra were used for the emission and excitation measurement, respectively.

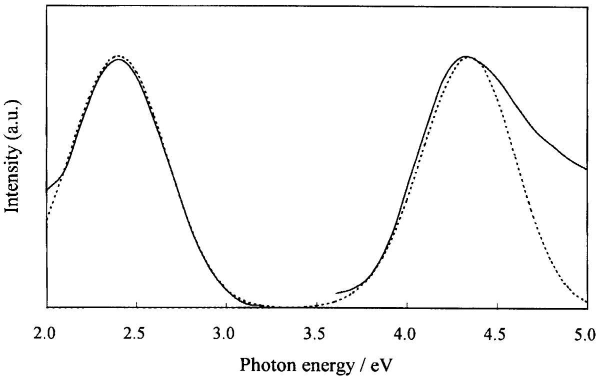

Fig. 3. Excitation and emission spectra of $CaMoO_4$ (—). (- - -) are calculated curves. The peak positions in the excitation and emission spectra were used for the emission and excitation measurement, respectively.

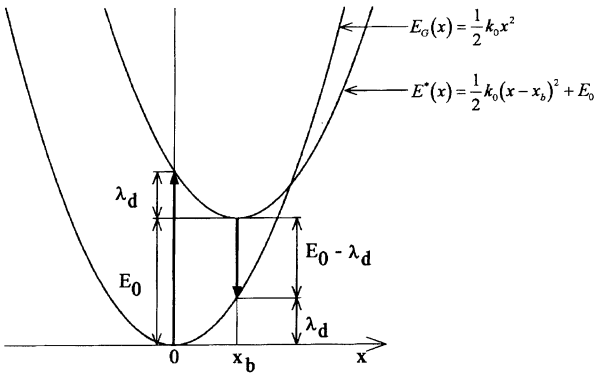

Fig. 4. A configurational coordinate diagram of tungstates and molybdates with the same force constant k_0.

of the $^3T_1$ excited state. λ_d, x, and x_b represent the reorganization energy, general potential coordinate, and coordinate at the potential minimum of the $^3T_1$ state, respectively. The reorganization energy represents the relaxation energy from the Franck–Condon state. It is well known that it plays an important role in electron-transfer reactions between molecules. This is the main reason for the Stokes shift in the excitation and emission spectra. In this model, it is assumed that the force constant of the excited state (k_0) is the same as that for the ground state. Under these assumptions, the transition energy ($h\nu$) between the $^1A_1$ and $^3T_1$ states is expressed as

$$h\nu = E^*(x) - E_G(x) = \frac{1}{2}k_0(x-x_b)^2 + E_0 - \frac{1}{2}k_0x^2, \qquad (1)$$

where the reorganization is defined as $\lambda_d = \frac{1}{2}k_0{x_b}^2$. Here,

$$x = \frac{-h\nu + \lambda_d + E_0}{k_0x_b} \qquad (2)$$

is obtained from Eq. 1. Since the luminescence is caused by the transition from the excited state to the ground state, the line shape of the emission spectrum reflects the distribution of the excited state. Here, the Boltzmann distribution is assumed for it, and the distribution is obtained as

$$p^*(x) = e^{-\frac{E^*(x)}{kT}} = e^{-\frac{k_0(x-x_b)^2+2E_0}{2kT}}, \qquad (3)$$

where k is the Boltzmann constant and T is the absolute temperature. If the maximum of $P^*(x)$ is to be equal to 1,

$$p^*(x) = e^{-\frac{k_0(x-x_b)^2}{2kT}} \qquad (4)$$

is obtained. When Eq. 2 is substituted into Eq. 4, Eq. 4 yields

$$p^*(h\nu) = e^{-\frac{(-h\nu+E_0-\lambda_d)^2}{4\lambda_d kT}}. \qquad (5)$$

Equation 5 represents the line shape of the emission spectrum from the excited state. As can be seen from Eq. 5, $p^*(h\nu)$ shows a maximum (=1) at $h\nu = E_0 - \lambda_d$. When the half width at half maximum is Δ/eV, we can obtain from Eq. 5

$$p^*(E_0 - \lambda_d + \Delta) = 0.5. \qquad (6)$$

Equations 5 and 6 along with $kT = 2.57 \times 10^{-2}$ eV at room temperature yield

$$\lambda_d = 14.0\Delta^2 \qquad (7)$$

$$(\lambda_d/\text{eV}, \Delta/\text{eV}).$$

The reorganization energy (λ_d) can be evaluated from Eq. 7 using the half width at half maximum of the observed emission spectra of the tungstates and molybdate. Since the peak position of the emission should be located at $h\nu = E_0 - \lambda_d$ (from Eq. 5), we can also evaluate E_0, i.e. the energy level of the triplet state from this relation, using the peak position of the emission spectra and the value of λ_d. The spectral shape of the excitation spectrum reflects the absorption process as well as the emission and radiationless processes. We assume that the excitation spectra of the tungstates and molybdate are based on the transition $^1A_1 \rightarrow {}^3T_1$.[8] The transition $^1A_1 \rightarrow {}^3T_1$ reflects the distribution of electrons at the ground state. The distribution of the ground state ($p_G(x)$) is given from Fig. 4, as

$$p_G(x) = e^{-\frac{k_0x^2}{2kT}}. \qquad (8)$$

By substituting Eq. 2 into Eq. 8, we obtain

$$p_G(h\nu) = e^{-\frac{(-h\nu+E_0+\lambda_d)^2}{4\lambda_d kT}}. \tag{9}$$

Equation 9 shows a theoretical expression for the absorption spectrum. In the present case, Eq. 9 is thought to represent the excitation spectra of the tungstates and molybdate. Equation 9 shows that $p_G(h\nu)$ takes the maximum at $h\nu=E_0+\lambda_d$. The half width at half maximum of $p_G(h\nu)$ is given by the following equation, which is the same as the case of emission spectrum Eq. 7 :

$$\lambda_d = 14.0\Delta^2 \tag{10}$$

$$(\lambda_d/\mathrm{eV},\ \Delta/\mathrm{eV}).$$

Equation 10 shows that the reorganization energy can be evaluated from the half width at half maximum of the excitation spectrum. From Eq. 9, the peak of the excitation is expected to be located at $h\nu=E_0+\lambda_d$. From this relation we can evaluate E_0, the energy level of the triplet state from the peak position of the excitation spectrum and λ_d. The energy level (E_0) and λ_d for each of the tungstates and molybdate were evaluated from the emission spectrum and the excitation spectrum of the corresponding tungstate and molybdate. The results are summarized in Table 1. As shown in this Table 1, the values of E_0, evaluated from the emission spectra of the tungstates, are close to those evaluated from the excitation spectra. However, the values of the reorganization energy, determined from the emission spectra, show a large difference amounting to ca. 1 eV, compared with those determined from the excitation spectra. From the above theory it is expected that the half width at half maximum of the emission spectrum is equal to that of the excitation spectrum. The experimental results show that the half width at half maximum of the emission spectra is larger than that of the excitation spectra in the case of the tungstates, as shown in Figs. 1, 2, and 3. Although the difference in the reorganization energies determined by the two methods is not large for $CaMoO_4$, the difference in E_0 is large, as shown in Table 1. This fact seems to indicate that the present model (Fig. 4) is too simple, because the force constant is the same k_0 at both the ground state and the excited state (triplet state).

The excited state of the tungstates are considered to be a charge-transfer state from 2p of O^{2-} to 5d of W^{6+} in $WO_4{}^{2-}$ ion.[1,5] This means that the ground state of $WO_4{}^{2-}$ can be expressed approximately as W^{6+}–O^{2-}, whereas the excited charge transfer state is expressed as W^{5+}–O^{-}. Therefore, it is thought that the Coulomb force between W and O weakens at the charge-transfer excited state. This is also true for the molybdates. Taking this into consideration, we modified the model (shown in Fig. 4). In the modified model, the force constants (k_1) at the excited charge-transfer state are assumed to be smaller than the force constant (k_0) at the ground state. The modified model is illustrated in Fig. 5. In this modified model, the potential energy at the ground state ($E_G(x)$) is

$$E_G(x) = \frac{1}{2}k_0x^2. \tag{11}$$

Table 1. Energy Level of Charge Transfer Triplet State E_0 and Reorganization Energies λ_d of Tungstates and $CaMoO_4$ Calculated from Excitation and Emission Spectra

	From excitation spectra		From emission spectra	
	E_0/eV	λ_d/eV	E_0/eV	λ_d/eV
$CaWO_4$	4.6	0.49	5.0	2.0
$MgWO_4$	3.9	0.48	4.0	1.5
$PbWO_4$	3.3	0.68	3.9	1.4
$ZnWO_4$	4.0	0.88	4.2	1.6
$CaMoO_4$	3.1	1.18	4.0	1.6

The potential energy at the excited state ($E^*(x)$) is given as

$$E^*(x) = \frac{1}{2}k_1(x-x_b)^2 + E_0. \tag{12}$$

For the transition between the two states,

$$h\nu = E^*(x) - E_G(x) = \frac{1}{2}k_1(x-x_b)^2 + E_0 - \frac{1}{2}k_0x^2. \tag{13}$$

Here, $h\nu$ represents the photon energy of the transition. By solving the quadratic equation of Eq. 13, we obtain

$$x = \frac{k_1x_b - \sqrt{k_1{}^2x_b{}^2 + 2(k_0-k_1)(\frac{1}{2}k_1x_b{}^2 + E_0 - h\nu)}}{k_1 - k_0}. \tag{14}$$

The distribution of the ground-state $p_G(h\nu)$ and the excited-state $p^*(h\nu)$ can be obtained by substituting Eq. 14 into Eqs. 4 and 8. $p^*(h\nu)$ and $p_G(h\nu)$ represent the line shape of the emission and excitation spectra of the tungstates and molybdate, respectively. We carried out a curve-fitting process for the emission and excitation spectra by a numerical calculation of $p^*(h\nu)$ and $p_G(h\nu)$, changing the values of the parameters (k_0, k_1, E_0, x_b). The results of the curve fitting are shown by dotted lines in Figs. 1, 2, and 3. The values of parameters E_0, λ_{d0}, λ_{d1}, obtained by the curve fitting, are summarized in Table 2. As can be seen by the dotted lines in Figs. 1, 2, and 3, the calculated $p^*(h\nu)$ agrees well with the emission spectra. Although the calculated $p_G(h\nu)$s are fitted well, especially at the rising shape of the excitation spectra, the fitting is not good, especially in the higher energy region of the spectra. This seems to indicate the existence of other excitation paths besides the $^1A_1 \rightarrow {}^3T_1$ transition in the

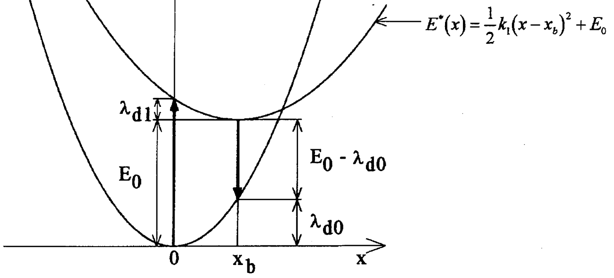

Fig. 5. A configurational coordinate diagram of tungstates and molybdates with different force constants k_0 and k_1.

Table 2. E_0, λ_{d0} and λ_{d1} of Tungstates and $CaMoO_4$ Calculated from Curve Fitting of the Excitation and the Emission Spectra

	E_0/eV	λ_{d0}/eV	λ_{d1}/eV
$CaWO_4$	4.40	1.44	0.72
$MgWO_4$	3.77	1.18	0.68
$PbWO_4$	3.43	0.89	0.53
$ZnWO_4$	3.68	1.05	0.62
$CaMoO_4$	3.50	1.10	0.85

higher energy region. The values of E_0 obtained by curve fitting are in the 4.4—3.5 eV range. The order of the magnitude is $CaWO_4 > MgWO_4 > ZnWO_4 > PbWO_4$. This order agrees well with that of the rising position of their excitation spectra, as well as the order of the peak position of the emission spectra. The values of the reorganization energy (λ_{d0}) are 1.05—1.44 eV, and those of λ_{d1} are 0.53—0.85 eV, as shown in Table 2. Although these values of λ_{d0} and λ_{d1} are much larger than the reorganization energy (ca. 0.1 eV) for the excitation and emission spectra of organic dyes, they are rather close to the reorganization energy of H^+ (1.5 eV) in an aqueous medium.[9] These large reorganization energies might be explained by a strong Coulomb interaction at the excited triplet state within the WO_4^{2-} and MoO_4^{2-} groups. It should be noted that those large reorganization energies can well explain the enormously large Stokes shifts observed for the excitation and emission spectra of those tungstates and molybdates.[1—5,7,8]

Conclusions

The spectral line shapes simulated by a configurational coordination model in which the force constant at the excited state is different from that at the ground state well explained the luminescence spectra and the line shape at the rising part of the excitation spectra of various tungstates and $CaMoO_4$ at room temperature. This result well supports our assumption that the excitation and emission of the tungstates and molybdates are based on the singlet-triplet transition. From a simulation of the spectral line shape (E_0), the energy levels of the excited triplet state and the reorganization energies at the ground state and the triplet state were determined. These results elucidated that the potential curve at the excited state becomes shallower than that at the ground state for these systems. They also well explained the large Stokes shifts observed for the luminescence for those compounds.

References

1) M. Morita, "Handbook of Fluorescent Materials," ed by Phosphor Research Society, S. Shionoya, Ohm Press, Tokyo (1987).

2) G. Blasse, K. C. Bleijenberg, and R. C. Powell, "Structure and Bonding 42," Springer-Verlag, Berlin and Heidelberg (1980).

3) G. Blasse and B. C. Grabmaier, "Luminescent Materials," Springer-Verlag, Berlin and Heidelberg (1994).

4) A. H. Kitai, "Solid State Luminescence," Chapman & Hall, London (1993).

5) S. P. McGlynn, T. Azumi, and D. Kumar, *Chem. Rev.*, **81**, 475 (1981).

6) R. Grasser and A. Scharmann, *J. Lumin.*, **12**, 473 (1976).

7) W. Walter and K. H. Butler, *J. Electrochem. Soc.*, **116**, 1245 (1969).

8) N. Saito, K. Kudo, and T. Sakata, *Bull. Chem. Soc. Jpn.*, **69**, 1241 (1996).

9) A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **78**, 1078 (1974).