Theoret. Chim. Acta (Berl.) 53, 95–99 (1979)

THEORETICA CHIMICA ACTA

Short Communication

Intensity Distribution in the Vibronic $\Gamma_7(^2T_{2g}) \rightarrow \Gamma_8(^4A_{2g})$ Transition of $ReBr_6^{2-}$ in Hexahalogenostannate Host Crystals*

Rainer Wernicke and Hans Kupka

Institut für Theoretische Chemie der Universität Düsseldorf, D-4000 Düsseldorf, Germany

The phosphorescence spectra of $ReBr_6^{2-}$ doped A_2SnX_6 (A = K, Rb, Cs; X = Cl, Br) have been measured at 10 K. The spectra consist of a weighted sum of progressions associated with the local modes of the $ReBr_6^{2-}$ center. By a fit to a generalized Lorentzian line shape function the totally symmetric distortion of the $\Gamma_7(^2T_{2g})$ excited state relative to the $\Gamma_8(^4A_{2g})$ ground state has been determined.

Key words: $ReBr_6^{2-}$ in hexahalogenostannate host crystals

1. Introduction

Up to the present time a great amount of luminescence data is available for hexahalogeno-complexes of transition metal ions. As in the case of octahedral $3d^3$ complexes, the major part of the observed intensity in the electronic transition arises from electric dipole terms. If the observed transitions occur between states belonging to the same strong field configuration, e.g. *d–d* t_{2g}^n–t_{2g}^n transitions, the low temperature emission spectra consist of a great number of sharp vibronic lines and a weak zero phonon line, the latter being a magnetic dipole transition [1–5]. The most intense lines correspond to the odd vibrational modes, the lines of weaker intensity are due to even vibrational modes of the complex octahedron. The latter presumably arise from a Jahn–Teller effect in the $^4T_{2g}$ state [6]. In addition to these lines there are some weak progressions in the totally symmetric mode based on these vibronic origins [6]. The rapid decrease of intensity within these progressions indicates that there is only a slight "displacement recoil" of total symmetry for the *d–d* transition, i.e. the equilibrium positions for the central ion and the surrounding

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* Dedicated to Professor Dr. H.-H. Schmidtke on the occasion of his 50th birthday.

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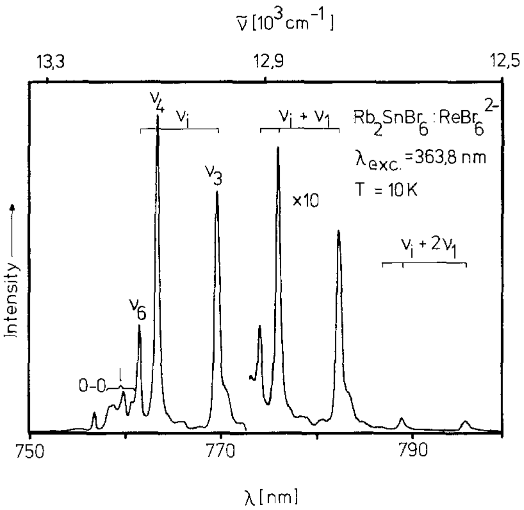

Fig. 1. Emission line shape of the phosphorescence associated with the $\Gamma_7(^2T_{2g}) \rightarrow \Gamma_8(^4A_{2g})$ transition of Rb_2SnBr_6:$ReBr_6^{2-}$ at 10 K

nuclei (ligands) are almost the same whether the central ion is in the ground or the excited electronic state and a small displacement along the totally symmetric mode $Q(a_{1g})$ is expected only. Since no large relaxation to the new equilibrium position of the nuclei is necessary, the cooperation of the totally symmetric vibration in the electronic transition is weak and the non-radiative electronic relaxation processes contribute a little to the widths of the observed lines. The emission spectra of $ReBr_6^{2-}$ doped A_2SnX_6 (A = K, Rb, Cs; X = Cl, Br) reported in this note are typical for such a weak coupling between electronic and nuclear motions. The emission (Fig. 1) corresponds to the transition from the higher-lying excited $\Gamma_7(^2T_{2g})$ state to the $\Gamma_8(^4A_{2g})$ ground state, both having the same electronic configuration t_{2g}^n and, therefore, a slight displacement of the electronic origins along the totally symmetric mode $Q(a_{1g})$. In the host crystals the $ReBr_6^{2-}$ complexes are loosely coupled to the lattice and, therefore, the phosphorescence is dominated by local modes rather than by impurity–lattice interactions. The lattice modes induce a little vibronic intensity [1] only.

2. Experimental Aspects

The hexahalo complexes and the mixed crystals were synthesized as described previously [1, 4].

The phosphorescence spectra were recorded photoelectrically on apparatus described elsewhere [4, 5].

3. Results and Discussion

Assuming a coupling scheme which includes the Re^{4+} ion and its nearest halogen ions and treating the surrounding medium as a heat bath, the electric dipole transition $\Gamma_7(^2T_{2g}) \rightarrow \Gamma_8(^4A_{2g})$ is given by a generalized Lorentzian line shape function [7, 8] which for y polarization, and considering the zero-temperature limit, is

$$W(\nu) = (2\nu^3/3\pi\hbar^2c^3) \sum_{\Gamma_u} \frac{\hbar}{2M_{\Gamma_u}\omega_{\Gamma_u}} \left[\sum_{\gamma_u} \sum_{\gamma_7,\gamma_8} |F_{y\Gamma_u\gamma_u}^{\gamma_7\rightarrow\gamma_8}|^2 \right]$$
$$\cdot \sum_{n=0}^{\infty} \frac{2\vartheta\hbar^{-1}}{(\nu - \Omega + \omega_{\Gamma_u} + n\omega_{a_{1g}}^{(g)} - \delta_\omega)^2 - (\vartheta\hbar^{-1})^2} I_1(n; \Delta_{a_{1g}}, \beta). \qquad (1)$$

The summation in Eq. (1) is over the three odd-parity modes (two T_{1u} and one T_{2u}) which can induce vibronic intensity, and over all members n in the progressions $\nu = \Omega - \omega_{\Gamma_u} - n\omega_{a_{1g}}^{(g)} + \delta_\omega$. Here $\hbar\Omega$ is the energy between the electronic origins and δ_ω the sum of the vibrational frequency differences between the excited (e) and ground (g) states. The single line possesses Lorentzian character with a relaxation width ϑ, which includes the effect of radiation damping, configuration mixing, interaction with vibrational modes of the more distant ions and other kinds of broadening mechanisms in the molecular eigenstates. Thus the lineshape (1) represents a weighted sum of progressions of Lorentzian components, each of them being associated with one of the vibronic origins $\nu_3(t_{1u})$, $\nu_4(t_{1u})$ and $\nu_6(t_{2u})$, respectively. The form of these progressions is determined by the intramolecular distribution $I_1(n; \Delta_{a_{1g}}, \beta)$ for the non-degenerate totally symmetric vibration a_{1g} given as [8]

$$I_1(n; \Delta_{a_{1g}}, \beta) = \frac{2\beta^{1/2}}{1+\beta} \sum_{k=0}^{[n/2]} (-1)^k \binom{-\frac{1}{2}}{k} \left(\frac{1-\beta}{1+\beta}\right)^{2k} I(n - 2k; \Delta_{a_{1g}}, \beta), \qquad (2)$$

with

$$I(m; \Delta_{a_{1g}}, \beta) = \exp\left(-\frac{\beta}{1+\beta}\Delta_{a_{1g}}^2\right) \left(\frac{1-\beta}{1+\beta}\right)^m \sum_{k=1}^{m} \frac{1}{k!} \binom{n-1}{n-k} \left(\frac{2\beta^2\Delta_{a_{1g}}^2}{1-\beta^2}\right)^k \qquad (3)$$

if $m \geqslant 1$, and

$$I(0; \Delta_{a_{1g}}, \beta) = \exp\left(-\frac{\beta}{1+\beta}\Delta_{a_{1g}}^2\right) \qquad (4)$$

if $m = 0$.

In Eqs. (2) to (4) $\Delta_{a_{1g}}$ is the origin displacement along the $Q(a_{1g})$ coordinate in units of $(\omega_{a_{1g}}M_{a_{1g}}/\hbar)^{1/2}$ and $\beta = \omega_{a_{1g}}^{(e)}/\omega_{a_{1g}}^{(g)}$ defines the change in frequency during the electronic transition. Other modes Γ for which $\Delta_\Gamma = 0$ contribute only little to the total strength of the transition and are omitted for the present analysis.

The weighted factors themselves, given by the coupling coefficients within the square brackets in Eq. (1) times the factors $\hbar/2M_{\Gamma_u}\omega_{\Gamma_u}$, determine the intensities of the vibronic origins ($n = 0$). They are generally functions of the octahedral vibrational frequencies and have been calculated elsewhere [9]. Taking the intensities of the combination lines relative to the intensities of the corresponding vibronic origins, the measured spectra of $ReBr_6^{2-}$ are compared with the theoretically determined line shape function (Eqs. (1–4)). The result for the progression built on the vibronic line $\nu_3(t_{1u})$ is given in Table 1, where for each spectrum the corresponding a_{1g} distortion $\Delta_{a_{1g}}$ and the frequency change β have been listed. The same results should obviously be obtained from the progressions associated with the

Table 1. Experimental and calculated intensities in the progressions $\nu_3(t_{1u}) + n\nu_1(a_{1g})$ of the emission spectra of $ReBr_6^{2-}$ centers in various host lattices. The intensities of the combination lines $\nu_3(t_{1u}) + n\nu(a_{1g})$ are expressed relative to the intensity of the corresponding vibronic origin $\nu_3(t_{1u})$

Crystals		Vibronic lines		
		$\nu_3 + \nu_1$	$\nu_3 + 2\nu_1$	$\nu_3 + 3\nu_1$
K_2SnBr_6	obs.	0.080	0.0045	0.00023
	calc.	0.081	0.0046	0.00022
	$(\Delta = 0.41, \beta = 0.97)$			
K_2SnCl_6	obs.	0.085	0.0050	0.00023
	calc.	0.085	0.0050	0.00024
	$(\Delta = 0.42, \beta = 0.97)$			
Rb_2SnBr_6	obs.	0.095	0.0059	0.00030
	calc.	0.093	0.0059	0.00030
	$(\Delta = 0.44, \beta = 0.97)$			
Cs_2SnBr_6	obs.	0.100	0.0060	0.00036
	calc.	0.098	0.0064	0.00034
	$(\Delta = 0.45\ \beta = 0.97)$			

vibronic origins $\nu_4(t_{1u})$ and $\nu_6(t_{2u})$. The width ϑ of the Lorentzians in Eq. (1) which simulate the experimental curves are found to be constant over the measured vibronic levels of the ground state.

According to the general belief, the vibrational frequency $\nu_1(a_{1g})$ decreases somewhat in the excited $\Gamma_7(^2T_{2g})$ state relative to that in the ground $\Gamma_8(^4A_{2g})$ state. The changes in frequency β are however greater than in the analogous case of $ReCl_6^{2-}$ radiating centers in similar hosts [6]. The decrease of the frequency factor β (from unity) indicates that the curvature of the excited adiabatic potential energy surface (APES) is smaller than that of the ground state. This lowering of the steepness of the APES can be attributed to a weaker bonding between the central Re^{4+} ion and its neighboring halogen ligands when the $ReBr_6^{2-}$ complex is excited to a higher electronic state.

From the Δ-parameter in Table 1 the absolute a_{1g} distortion $\Delta Q(a_{1g}) = \Delta_{a_{1g}}(\hbar/\omega_{a_{1g}}M_{a_{1g}})^{1/2}$ is obtained to be 0.0177–0.0195 Å depending on the host (the sign of $\Delta Q(a_{1g})$ is positive). This produces an expansion of the Re–Br bond length along the three octahedral axes of about $\Delta x = \Delta y = \Delta z = (1/\sqrt{6})\,\Delta Q(a_{1g}) = 0.0075$ Å. Analogous results were found in the case of $ReCl_6^{2-}$ centers in similar hosts [6]. The accuracy of the estimates of $\Delta Q(a_{1g})$ and consequently of Δx is limited by the experimental error in determining the intensities of the vibronic lines in the progressions and is assumed to be 5%.

Finally, we point out that each of the vibronically induced magnetic dipole transitions $\nu_1(a_{1g})$ and $\nu_2(e_g)$ of the $ReBr_6^{2-}$ octahedron acts also as an origin for a progression in $\omega_{a_{1g}}^{(g)}$. The form of these progressions is also expressed in terms of

Eqs. (2)–(4). Since these series of lines are much weaker than those of the electric dipole lines, they are observed experimentally up to the number $n = 1$ only.

Acknowledgements. We are grateful to the Deutsche Forschungsgemeinschaft for financial support. We would also like to thank Mrs. Niegeloh for assistance in the laboratory and Mr. Degen for the computer calculations.

References

1. Schmidtke, H.-H., Wernicke, R.: Chem. Phys. Letters **40**, 339 (1976)
2. Brittain, H. G., Richardson, F. G., Jasinski, J. P., Jeakel, W. C., Schatz, P. N.: J. Phys. Chem. **80**, 2228 (1976)
3. Black, A. M., Flint, C. D.: J. Chem. Soc. Faraday II **73**, 877 (1977)
4. Wernicke, R., Schmidtke, H.-H.: Mol. Phys. **37**, 607 (1979)
5. Wernicke, R., Eyring, G., Schmidtke, H.-H.: Chem. Phys. Letters **58**, 267 (1978)
6. Kupka, H., Enßlin, W., Wernicke, R., Schmidtke, H.-H.: Mol. Phys., in press
7. Kupka, J.: Chem. Phys. Letters **41**, 114 (1976)
8. Kupka, H.: Mol. Phys. **36**, 685 (1978)
9. Kupka, H., Wernicke, R., Enßlin, W., Schmidtke, H.-H.: Theoret. Chim. Acta (Berl.) **51**, 297 (1979)

Received April 26, 1979