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## COMMENT

# Analysis of $\text{Cr}^{3+}$ optical parameters: an appraisal of the method by Luo and Huang

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**Abstract.** The method reported by Luo and Huang (*J. Phys.: Condens. Matter* 1993 5 9411) for analysing the optical data of  $\text{Cr}^{3+}$  complexes, which uses only a coupling to one single vibrational mode is discussed. Taking as a guide the case of the  $\text{CrF}_6^{3-}$  complex it is pointed out firstly that the frequency  $\omega$  used in the method has no direct physical meaning, being smaller than those associated with  $A_{1g}$  and  $E_g$  modes observed in optical spectra, and secondly that the assumed relation between  $10Dq$  and the Stokes shift  $E_S$  is in general not true as it is only valid for the *partial* contribution of the  $A_{1g}$  mode to  $E_S$ . Despite these facts it is also explained that no unreasonable band-width values can be predicted provided that the *fitted* values of the Huang–Rhys factor and the frequency reproduce the experimental Stokes shift. In conclusion the proposed method of Luo and Huang is shown to be not conceptually right, giving rise to a worse description than that achieved through the coupling to the two  $A_{1g}$  and  $E_g$  modes of the  $\text{CrF}_6^{3-}$  complex.

## 1. Introduction

In a very recent paper, Luo and Huang [1] proposed a method for calculating the Huang–Rhys factor  $S$  the frequency  $\omega$  and the band width  $W$  associated with the  ${}^4T_2 \rightarrow {}^4A_2$  band of the  $\text{Cr}^{3+}$  impurity in several fluoride and oxide host lattices. This information is extracted only from the experimental peak energies of absorption ( $E_a$ ) and emission ( $E_e$ ) bands and is partially based on a recent paper by the present authors [2].

Although Luo and Huang claim that through their method ‘the calculated values agreed very well with the experimental data’, we believe, however, that this conclusion together with the foundations of the proposed method need to be revised according to the arguments given in the following section.

## 2. Discussion

Luo and Huang [1] try to describe the Stokes shift  $E_S$  and the band width  $W$  through a linear electron–phonon coupling involving *only one* effective mode and so  $E_S$  and  $W$  are given by

$$E_S = 2S\hbar\omega \quad (1)$$

$$W = 2.36S^{1/2}\hbar\omega[\coth(\hbar\omega/2kT)]^{1/2}. \quad (2)$$

Although historically this expression has been used as a simple model for explaining the Stokes shift and band widths of transition-metal ions, experimental data on  ${}^4T_2 \rightarrow {}^4A_2$  bands of  $\text{CrX}_6^{3-}$  complexes (X=halide) [3–6] clearly reveal that a proper microscopic description of  $E_S$  and  $\omega$  involves the linear coupling to two modes of the complex. Such modes are the symmetric  $A_{1g}$  and the Jahn–Teller  $E_g$  modes. Both modes display a *stretching* character and are allowed for an orbital triplet state under linear coupling conditions.

Therefore a more realistic microscopic understanding of  $E_S$  and  $W$  (at 0 K) can be made through

$$E_S = E_S^0 + \Delta E_u$$

$$E_S^0 = S_A \hbar \omega_A + S_E \hbar \omega_E \quad (3)$$

$$\Delta E_u = 2\hbar \omega_u$$

$$W = 2.36[S_A(\hbar \omega_A)^2 + S_E(\hbar \omega_E)^2]^{1/2}. \quad (4)$$

In (3) and (4),  $\omega_A$  and  $\omega_E$  are associated with the  $A_{1g}$  and  $E_g$  modes, respectively. The contribution  $\Delta E_u$  containing the odd phonon of frequency  $\omega_u$  appears because the  ${}^4T_2 \rightarrow {}^4A_2$  transition is parity forbidden. At higher temperatures such a contribution should be replaced by

$$\Delta E_u = 2\hbar \omega_u \tanh(\hbar \omega_u / 2kT). \quad (5)$$

To relate  $S$  and  $\omega$  involved in equation (1), Luo and Huang make use of the relation

$$2S\hbar\omega = (n^2\hbar^2/6MR^2)(E_a/\hbar\omega)^2 \quad (6)$$

following the analysis made in [2]. In (6),  $M$  is the ligand mass,  $R$  the  $\text{Cr}^{3+}$ –ligand distance and  $n$  reflects the dependence of  $10Dq$  upon  $R$  through the law

$$10Dq = KR^{-n}. \quad (7)$$

The relation which was actually proposed in [2] reads, *however*, as follows:

$$2S_A \hbar \omega_A = (n^2 \hbar^2 / 6MR^2)(10Dq / \hbar \omega_A)^2 \quad (8)$$

where, for the  ${}^4T_2$  state of  $\text{CrX}_6^{3-}$ ,  $10Dq = E_a$ . Experimental results on systems containing  $\text{Mn}^{2+}$  and  $\text{Cr}^{3+}$  impurities lead to values of the exponent  $n$  close to five [2]. Therefore equation (8) relates  $\hbar \omega_A$  *only to a fraction* of the Stokes shift (called simply  $E_{SA}$ ) and not to the total Stokes shift  $E_S$  such as it is made through (6). For  $\text{Cr}^{3+}$  in elpasolites the fraction  $E_{SA}/E_S^0$  is about 60% [2]. Owing to this the use of (1) and (6) (instead of (3) and (8)) in the analysis of the experimental Stokes shift  $E_S$  leads to an  $\omega$ -value which has no direct physical meaning. In fact,  $\omega$  must be smaller than  $\omega_A$  and also it can be smaller than  $\omega_E$ .

To be more specific, let us consider the case of  $\text{K}_2\text{NaGaF}_6:\text{Cr}^{3+}$  where  $\hbar \omega_A = 570 \text{ cm}^{-1}$  and  $\hbar \omega_E = 480 \text{ cm}^{-1}$  measured through emission spectra [6, 7]. Using equations (1) and (5) to analyse the RT experimental values  $E_a = 16000 \text{ cm}^{-1}$  and  $E_e = 13200 \text{ cm}^{-1}$ , it leads to  $\hbar \omega \simeq 380 \text{ cm}^{-1}$  and  $S = 3.8$ . Therefore, the analysis proposed by Luo and Huang leads to an  $\omega$ -value which is certainly much smaller than the two frequencies  $\omega_A$  and  $\omega_E$  with *direct physical* meaning.

Moreover, to compensate this underestimation of  $\omega$  with respect to the experimental  $\omega_A$  and  $\omega_E$ -values the analysis based on the coupling to a single mode leads to an overestimation of  $S$  with respect to  $S_A$  and  $S_E$ . For  $\text{K}_2\text{NaGaF}_6\cdot\text{Cr}^{3+}$  taking  $n = 4.6$  [6] it is found from (7) that  $S_A = 1.3$ . Also we have recently calculated the value of  $S_E$  and its dependence on the metal–ligand distance for  $\text{CrF}_6^{3-}$ . Writing the electron–phonon coupling with the Jahn–Teller mode  $E_g$  for the electronic  ${}^4T_2$  state as

$$H_{e,\text{ph}}(E_g) = V_E(Q_\theta \mathbf{U}_\theta + Q_\epsilon \mathbf{U}_\epsilon) \quad (9)$$

where the  $3 \times 3$  matrices  $\mathbf{U}_\theta$  and  $\mathbf{U}_\epsilon$  are given by

$$\mathbf{U}_\theta = \begin{bmatrix} 1/2 & 0 & 0 \\ 0 & 1/2 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad \mathbf{U}_\epsilon = \begin{bmatrix} -\sqrt{3}/2 & 0 & 0 \\ 0 & \sqrt{3}/2 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (10)$$

then  $S_E$  and the related Jahn–Teller energy  $E_{JT}$  are given by

$$E_{JT} = S_E \hbar \omega_E = V_E^2 / 2\mu\omega_E^2. \quad (11)$$

First self-consistent charge extended Hückel and  $\text{MS-X}_\alpha$  calculations for the  ${}^4T_2$  state of  $\text{CrF}_6^{3-}$  computed at an equilibrium value  $R = 1.91 \text{ \AA}$  lead to  $V_E = -130 \text{ cm}^{-1} \text{ pm}^{-1}$  and  $V_E = -107 \text{ cm}^{-1} \text{ pm}^{-1}$ , respectively. Thus taking  $V_E = -118 \text{ cm}^{-1} \text{ pm}^{-1}$  and using  $\hbar\omega_E = 480 \text{ cm}^{-1}$  from the experimental data for  $\text{K}_2\text{NaGaF}_6\cdot\text{Cr}^{3+}$  it is found that  $S_E = 1.1$  and  $E_{JT} = 530 \text{ cm}^{-1}$ . The latter value is comparable with that recently reported by Bartram and co-workers [17] for  $\text{CrX}_6^{3-}$  ( $X = \text{F}^-$  or  $\text{Cl}^-$ ) and supports the fact that  $S_E$  is close to unity. Furthermore, in  $\text{Rb}_2\text{KGaF}_6\cdot\text{Cr}^{3+}$ , vibronic progressions due to the  $E_g$  mode are especially well observed in the low-temperature spectrum. From the experimental intensities a value  $S_E = 1.2$  has been inferred [8]. Thus from all these arguments it can be said that the  $S$ -value determined through the method proposed by Lou and Huang is about 1.8 times higher than  $S_A + S_E$ .

As good proof for supporting their method, Lou and Huang point out, however, that reasonable predictions of the band width  $W$  can be achieved using equation (2) and the values of  $S$  and  $\omega$  derived from (1) and (6). This assertion has to be viewed with caution for the following reasons.

(1) Although the interpretation of the measured  $E_S$ - and  $W$ -values through the coupling with both  $A_{1g}$  and  $E_g$  is in agreement with experimental facts (in particular with the vibrational progressions observed in the optical spectra) and with theoretical calculations it is also true that an *equivalent* (but physically meaningless) description can always be made using only one mode. We shall denote  $\bar{S}$  and  $\bar{\omega}$  the Huang–Rhys factor and the frequency of the single mode obtained by *fitting* the experimental  $E_S$  and  $W$  through (1) and (2).

Moreover, taking into account the experimental uncertainties in both  $E_S$  and  $W$  (being around 10%) there are in practice *several*  $\{S, \omega\}$ -values leading to calculated  $E_S$ - and  $W$ -values which are acceptable. Furthermore, as pointed out in equation (3), to extract Huang–Rhys factors from the experimental  $E_S$  one needs to subtract the contribution coming from the odd-phonon assistance. This is not considered in equation (1) and can modify the  $E_S^0$ -value by about 6% at room temperature if  $\hbar\omega_u = 200 \text{ cm}^{-1}$ . Therefore, we can say that values  $S \simeq 3$  and  $\hbar\omega = 450 \text{ cm}^{-1}$  can also be compatible with the experimental  $E_S$ - and  $W$ -values for  $\text{CrF}_6^{3-}$  systems.

(2) Neglecting now these uncertainties in  $W$  and  $E_S^0$  the values of  $S$  and  $\omega$  derived through (1) and (6) are not necessarily equal to  $\bar{S}$  and  $\bar{\omega}$ . Thus the calculated value of  $W_c$

using (1), (6) and (2) and the experimental  $E_c$  and  $E_a$  data would be in principle different from the correct value of  $W$ . Nevertheless, calling  $\delta\omega = \omega - \bar{\omega}$  and  $\delta W = W_c - W$ , it can easily be demonstrated that to a first approximation at 0 K the relation

$$\delta W/W = \frac{1}{2}\delta\omega/\bar{\omega} \quad (12)$$

holds *provided that*  $S$  and  $W$  are *always* connected by equation (1) to the experimental Stokes shift. Thus, even if  $\delta\omega = 120 \text{ cm}^{-1}$  and  $\hbar\bar{\omega} = 450 \text{ cm}^{-1}$ , then  $\delta W/W = 15\%$ . This explains that the calculated  $W_c$ -value is not far from the correct value of  $W$  although the model used is physically meaningless.

In conclusion the present reasoning indicates that the scheme proposed by Lou and Huang does not improve conceptually a more rigorous description based on the coupling to the  $A_{1g}$  and  $E_g$  stretching modes of the complex well observed in experimental optical spectra. The extension of equation (8) (reported in [2]) giving rise to (6) (which is in principle not justified) and the fact that  $\omega$ -values with no direct physical meaning are obtained are among the main drawbacks emphasized through the present work.

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