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Resonant excitation energy transfer in $[Rh(bpy)_3][NaCr(ox)_3]ClO_4$

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Abstract

Resonant fluorescence line narrowing of the R_1 line of the $[Cr(ox)_3]^{3-}$ chromophore in $[Rh(bpy)_3][NaCr(ox)_3]ClO_4$ at 1.6 K neither gives rise to the usual three-line pattern nor to spectral diffusion. Instead multi-line spectra with spacings equal to the zero-field splitting of the ground state are observed. This phenomenon is attributed to efficient non-radiative *resonant* energy transfer within the R_1 line.

Fluorescence line narrowing (FLN) spectroscopy is a powerful method for probing the homogeneous linewidth of optical transitions in the solid state and can provide valuable information on the dynamics of relaxation processes [1]. In particular, applied to coordination compounds of transition metals, unambiguous assignments concerning their electronic structure have been possible [2].

Fig. 1 shows resonant FLN spectra at 1.6 K of a microcrystalline sample of $[Rh(bpy)_3]$-$[NaCr(ox)_3]$-ClO_4 (bpy = 2,2′-bipyridine, ox = oxalate) for different excitation wavelengths within the inhomogeneously broadened R_1 line [3] of the $[Cr(ox)_3]^{3-}$ chromophore. The experimental apparatus, using a scanning Fabry–Perot interferometer (Burleigh RC-110) and a CW dye laser (Spectra Physics 375) operating at single frequency, is described in Ref. [4]. Both the number of lines observed as well as their relative intensities depend strongly upon the excitation wavelength. The non-selectively excited, inhomogeneously broadened emission centred at $\tilde{\nu}_0 = 14400\ cm^{-1}$ [6] and the instrumental lineshape are included in Fig. 1.

At 1.6 K three levels of Cr^{3+} have to be considered: The two zero-field components of the $^4A_2$ ground state (g_a and g_b) and the low-energy component of the ^2E state (e). The higher energy component of the ^2E state is not populated at that temperature as the splitting is 13 cm^{-1} [6]. Because the inhomogeneous linewidth $\Gamma_{inh} = 3.8\ cm^{-1}$ (FWHM) is larger than the zero-field splitting of the $^4A_2$ ground state $D = 1.3\ cm^{-1}$ and the homogeneous linewidth $\Gamma_{hom} = 0.012\ cm^{-1}$ (FWHM) [7], a three-line pattern would be expected in the FLN spectrum, with sidebands at $\pm D$ from the resonant line [1]. Three-line patterns have been observed in a number of Cr^{3+} systems where luminescence occurs from the ^2E state, such as Al_2O_3:Cr^{3+} [8–10] and the

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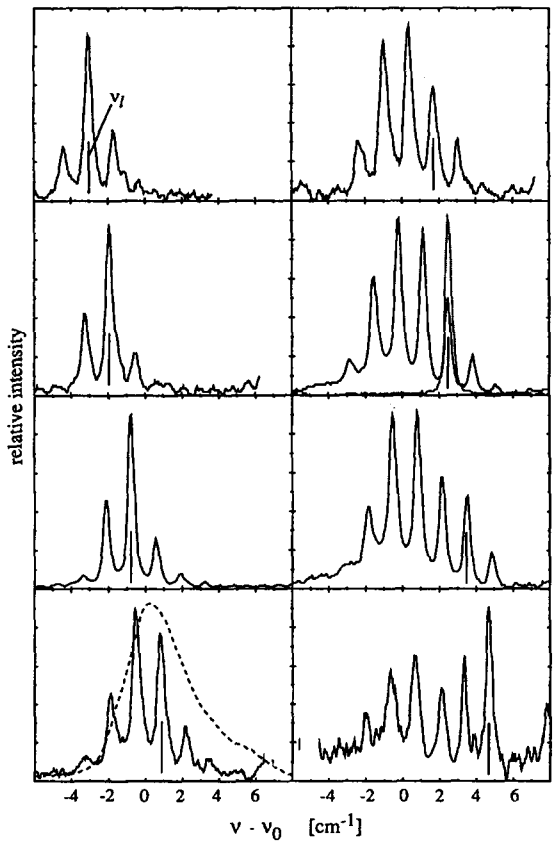

Fig. 1. Resonant FLN spectra of $[Rh(bpy)_3][NaCr(ox)_3]ClO_4$ at 1.6 K as a function of the laser frequency $\tilde{\nu}_l$ within the inhomogeneous width of the R_1 transition. The central frequency of the inhomogeneous distribution $\tilde{\nu}_0 = 14400$ cm^{-1}, $\Gamma_{inh} = 3.8$ cm^{-1}. The instrumental lineshape (· · ·) and the inhomogeneous emission (– – –) are also shown. The free spectral range of the Fabry–Perot interferometer was 9.75 cm^{-1}.

tris-chelate complexes $[Cr(bpy)_3]^{3+}$ [2,4,5] and $[Cr(ox)_3]^{3-}$ [7] in weakly doped crystalline systems and glasses.

Energy transfer within the ^2E state is a common phenomenon in not too dilute systems. It is usually observed in FLN experiments as temperature dependent spectral diffusion [9,10] and is thus a phonon-assisted process [10,11]. The multi-line spectra of the neat title compound $[Rh(bpy)_3][NaCr(ox)_3]ClO_4$ call for a different explanation. The model presented in the following postulates a *resonant* energy transfer process.

Fig. 2 depicts the basic assumptions of the model. The inhomogeneous distribution of transition energies is given by a Gaussian. As is normal in an FLN experiment with two inhomogeneously broadened and overlapping transitions, two sets of molecules are excited when irradiating at a given laser frequency $\tilde{\nu}_l$ within the inhomogeneous envelope: a set denoted $i = 0$, for which the transition $g_a \rightarrow e$ is resonant ($\tilde{\nu}_{a0} = \tilde{\nu}_l$), and a set denoted $i + 1 = 1$, for which the transition $g_b \rightarrow e$ is resonant ($\tilde{\nu}_{b1} = \tilde{\nu}_l$). Resonant energy transfer is possible within these subsets individually. However, because each subset has two transitions and Γ_{inh} is larger than D there are additional resonant processes possible, for instance, from the subset $i = 0$ to the subset $i - 1 = -1$, for which the $g_a \rightarrow e$ transition is resonant with the $g_b \rightarrow e$ transition on subset $i = 0$, or from subset $i = 1$ to subset $i + 1 = 2$, for which the $g_b \rightarrow e$ transition is resonant with the $g_a \rightarrow e$ transition on subset $i = 1$. This results in a ladder spaced by D within the inhomogeneous band, with *resonant* energy transfer processes between spectral neighbours i and $i \pm 1$. The following set of differential equations describes this situation:

$$\frac{dN_{ei}}{dt} = -N_{ei}(k_0 + k_{et}(N_{ai-1} + N_{bi+1})) + k_{et}(N_{ei+1}N_{ai} + N_{ei-1}N_{bi}) + \delta_{0i}k_a^{ex}N_{ai} + \delta_{1i}k_b^{ex}N_{bi}, \quad (1)$$

In Eq. (1) $k_0 = k_a + k_b$ is the sum of the individual radiative rate constants of the two transitions, k_a^{ex} and k_b^{ex} are the excitation rate constants for the two transitions, for which the relation $k_a^{ex}/k_b^{ex} = k_a/k_b$ holds, N_{ai}, N_{bi} and N_{ei} are the populations of the three levels in set i, k_{et} is the bimolecular energy transfer rate constant and δ is the delta function. The possibly small dependences of k_a and k_b, and thus of k_a^{ex} and k_b^{ex}, on the exact excitation energy within the inhomogeneous distribution are neglected.

As no evident transient hole burning was observed at the low laser powers used, $N_{ei} \ll N_{ai}$, N_{bi} is assumed. Therefore $N_{ai} + N_{bi} \approx N_{0i}$ holds, where N_{0i} is the total number of complexes in subset i. Furthermore, assuming a comparatively fast spin–

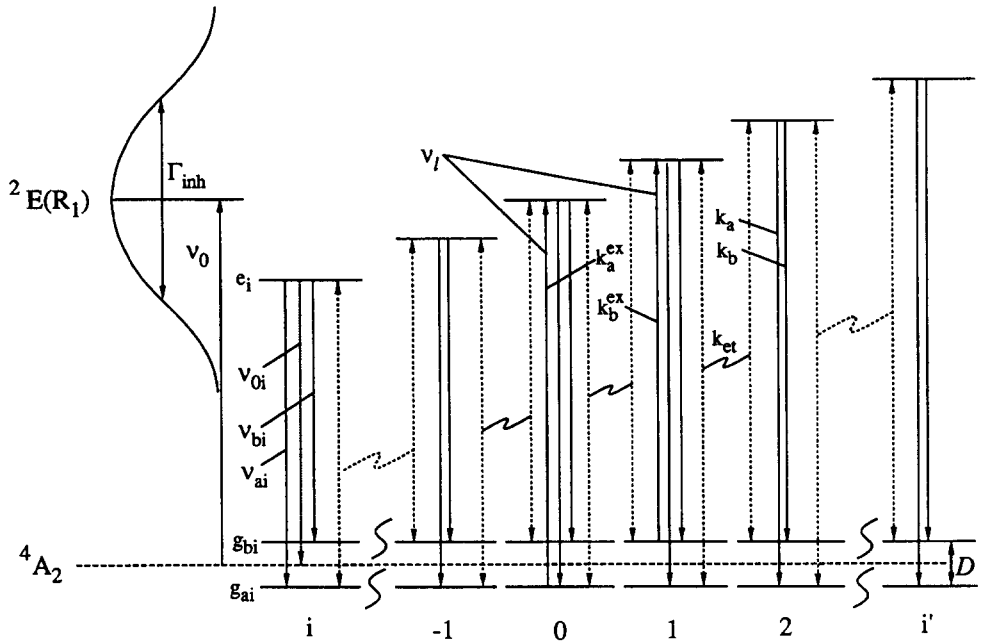

Fig. 2. Schematic representation of the model for *resonant* energy transfer within the R_1 transition of Cr^{3+}.

lattice relaxation time for the ground state, N_{ai} and N_{bi} are given by a Boltzmann distribution:

$$N_{ai} = N_{0i}/(1 + \exp(-D/k_B T))$$

and

$$N_{bi} = N_{0i} \exp(-D/k_B T)/(1 + \exp(-D/k_B T)). \quad (2)$$

The values for N_{0i}, in turn, are determined by the Gaussian distribution:

$$N_{0i}(\tilde{\nu}_{0i}) = N_0 \exp\left\{ -\frac{4 \ln 2 (\tilde{\nu}_{0i} - \tilde{\nu}_0)^2}{\Gamma_{inh}^2} \right\}, \quad (3)$$

where N_0 is the density of complexes within a homogeneous linewidth at the center of the distribution. The central frequency and the corresponding emission frequencies of the ith member in the sequence are given by:

$$\tilde{\nu}_{0i} = (\tilde{\nu}_{ai} + \tilde{\nu}_{bi})/2$$

$$\tilde{\nu}_{ai} = \tilde{\nu}_l + iD$$

$$\tilde{\nu}_{bi} = \tilde{\nu}_{ai} - D.$$

In the steady state, the differential Eqs. (1) are reduced to a set of linear equations which are straightforward to solve numerically for N_{ei}. The resulting FLN spectrum can be calculated as follows:

$$I(\tilde{\nu}) \sim \sum_i N_{ei} \{ k_a g(\tilde{\nu}_{ai}) + k_b g(\tilde{\nu}_{bi}) \}, \quad (5)$$

where $g(\tilde{\nu})$ is the instrumental lineshape included in Fig. 1.

Sample calculations were performed with the following parameters fixed at the values obtained on [Ru(bpy)$_3$][NaAl:Cr(0.1%)(ox)$_3$] [7]: $D = 1.3$ cm^{-1}, $k_0 = 700$ s^{-1}, $k_a/k_b = k_a^{ex}/k_b^{ex} = 2.5$, $\Gamma_{hom} = 0.012$ cm^{-1}, and for the title compound [Rh(bpy)$_3$]-[NaCr(ox)$_3$]ClO$_4$ [6,7]: $\Gamma_{inh} = 3.8$ cm^{-1}, $N_{tot} = 10^{21}$ cm^{-3}, respectively. N_{tot} is the total density of chromophoric units. With the above values the density of complexes within a homogeneous bandwidth at the central frequency of the inhomogeneous distribution is estimated to be:

$$N_0 = 2 \frac{\Gamma_{hom}}{\Gamma_{inh}} N_{tot} = 6 \times 10^{18} \text{ cm}^{-3}. \quad (6)$$

In addition, the temperature was set to the experimental value: $T = 1.6$ K, and the instrumental resolution to: $\Delta\tilde{\nu}_r = 0.4$ cm^{-1}.

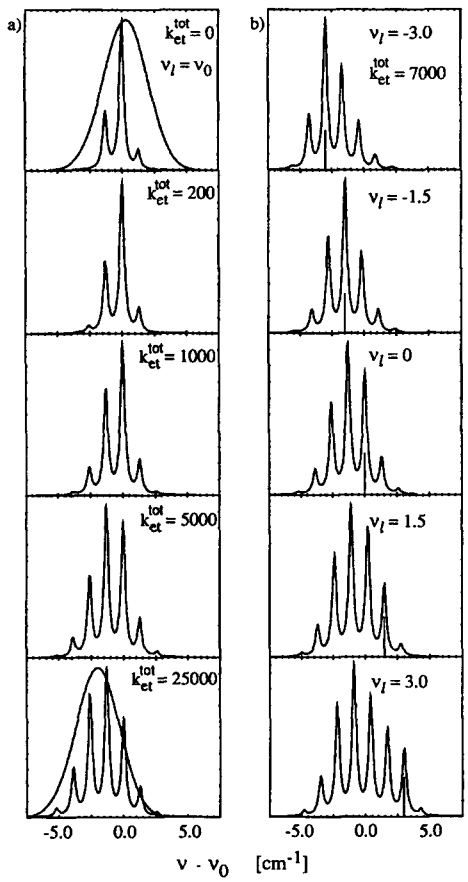

Fig. 3. Simulated resonant FLN spectra using parameters relevant for the $[Cr(ox)_3]^{3-}$ chromophore given in the text. (a) As a function of the total energy transfer rate constant k_{et}^{tot} and $\tilde{\nu}_l = \tilde{\nu}_0$. Included are the inhomogeneous lineshapes expected for no energy transfer (top panel) and fast energy transfer (bottom panel). (b) As a function of excitation frequency $\tilde{\nu}_l$ and $k_{et}^{tot} = 7 \times 10^3$ s^{-1}.

This leaves the energy transfer rate constant k_{et} as the only free parameter, and accordingly Fig. 3a shows the simulated FLN spectra for different values of k_{et}, or rather for the more relevant quantity the pseudo first order rate constant $k_{et}^{tot} = k_{et} \cdot N_0$, and with the laser frequency $\tilde{\nu}_l$ set equal to $\tilde{\nu}_0$. With $k_{et}^{tot} = 0$, the straightforward three-line pattern within the Gaussian distribution results (top panel). As k_{et}^{tot} is increased additional lines appear on either side of the three original lines, spaced by the zero-field splitting of the ground state. As long as k_{et}^{tot} is smaller than k_0, the line which is resonant with $\tilde{\nu}_l$ is still the most intense, but as k_{et}^{tot} becomes larger than k_0, the additional lines on the low-energy side become more intense, until for very large k_{et}^{tot} the envelope of the spectrum is given by a Boltzmann distribution of the i levels weighted by the Gaussian distribution (bottom panel).

In a second simulation k_{et}^{tot} is held constant at 7×10^3 s^{-1}, and the laser frequency is varied within the inhomogeneous line. The resulting profiles, shown in Fig. 3b, reproduce the experimental dependence on the laser frequency $\tilde{\nu}_l$ quite well, including the profiles for excitation into the wings. With $k_0 =$ 700 s^{-1}, the *resonant* energy transfer is thus an order of magnitude faster than the radiative relaxation of the single ions.

In principle, k_{et} depends upon the exact distance distribution of acceptors around any given excited donor and is thus distributed around some mean value rather than a constant. However, resonant energy transfer within a given subset is just as efficient as between subsets. Although this does not explicitly appear in Eq. (1), it results in sufficient local averaging to justify the above approach with k_{et} having the same value for all donors.

The quest for *resonant* energy transfer within the R_1 line of Cr^{3+}, in particular in ruby, Al_2O_3:Cr^{3+}, has been long and the results controversial (for a full discussion see Ref. [1]). The FLN experiments on Al_2O_3:Cr^{3+}(0.9%) of Selzer and coworkers [9,10] indicate that single ion to single ion energy transfer proceeds mainly via spectral diffusion, i.e. via a phonon-assisted process showing a typical linear dependence of the transfer rate with temperature [12]. Somewhat later Chu et al. [13] and Jessop and Szabo [14] succeeded in observing slow resonant single ion energy transfer based on electric field experiments at liquid helium temperature. The transfer times on a millisecond timescale are compatible with a dipole–dipole mechanism. $[Rh(bpy)_3][NaCr(ox)_3]ClO_4$ crystallises in a cubic space group, and the $[Cr(ox)_3]^{3-}$ complexes sit on trigonal lattice sites, which are all equivalent in the absence of external fields [6]. There are two reasons for the faster *resonant* process in this system. (a) Because this is not a doped system and because of the more than one order of magnitude larger homogeneous linewidth (0.012 cm^{-1} versus < 0.001 cm^{-1} [15]), the concentration of centres which are resonant with each other is more than an order of magnitude larger than in ruby doped with

0.9% Cr^{3+}. (b) With a radiative lifetime of 1.4 ms, as opposed to 3.5 ms for ruby, the oscillator strength f of the $^4A_2 \rightarrow {}^2E$ transition in the $[Cr(ox)_3]^{3-}$ chromophore is larger by a factor of 2.5. The somewhat smaller inhomogeneous linewidth in ruby (1.8 cm^{-1} at 0.9% doping level [10]) counteracts the above to some extent, but cannot override their combined effect.

Following Refs. [16] and [17], the critical distance R_c for which the rate of resonant energy transfer via a dipole–dipole mechanism is equal to the radiative decay rate of the single ions can be estimated to be ≈ 45 Å on the basis of the oscillator strength f of the R_1 line of 6×10^{-7} [6] and the above homogeneous linewidth. On average, an excited complex at the centre of the inhomogeneous distribution will have ≈ 6 complexes to which resonant energy transfer is possible, within this radius. This is sufficient to guarantee the experimentally observed energy transfer rates. Radiative processes can be excluded on the basis of an absorption cross section at the maximum of the inhomogeneous distribution of $\approx 7 \times 10^{-20}$ cm^2 and a crystallite size of less than 10 μm.

We conclude that in $[Rh(bpy)_3][NaCr(ox)_3]ClO_4$ energy transfer within the R_1 line of the ^2E state is a *resonant* process at 1.6 K. Preliminary observations point towards a phonon-assisted process taking over at temperatures above 3.5 K. Time-resolved FLN experiments are needed to disentangle the two processes and work is in progress accordingly.

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