

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/243859626>

Effect of External Pressure on the Excitation Energy Transfer from $[\text{Cr}(\text{ox})_3]^{3-}$ to $[\text{Cr}(\text{bpy})_3]^{3+}$ in $[\text{Rh}_{1-x}\text{Cr}_x(\text{bpy})_3][\text{NaM}_{1-y}\text{Cr}_y(\text{ox})_3]\text{ClO}_4$

ARTICLE in CHEMPHYSCHEM · OCTOBER 2010

Impact Factor: 3.42

READS

36

3 AUTHORS, INCLUDING:



Prodipta Pal

University of Geneva

6 PUBLICATIONS 31 CITATIONS

SEE PROFILE

Effect of External Pressure on the Excitation Energy Transfer from $[\text{Cr}(\text{ox})_3]^{3-}$ to $[\text{Cr}(\text{bpy})_3]^{3+}$ in $[\text{Rh}_{1-x}\text{Cr}_x(\text{bpy})_3][\text{NaM}_{1-y}\text{Cr}_y(\text{ox})_3]\text{ClO}_4$

Mia Milos, Prodipta Pal, and Andreas Hauser^{*[a]}

Resonant excitation energy transfer from $[\text{Cr}(\text{ox})_3]^{3-}$ to $[\text{Cr}(\text{bpy})_3]^{3+}$ in the doped 3D oxalate networks $[\text{Rh}_{1-x}\text{Cr}_x(\text{bpy})_3][\text{NaM}_{1-y}\text{Cr}_y(\text{ox})_3]\text{ClO}_4$ ($\text{ox} = \text{C}_2\text{O}_4^{2-}$, $\text{bpy} = 2,2'$ -bipyridine, $\text{M} = \text{Al}$, Rh) is due to two types of interaction, namely super exchange coupling and electric dipole–dipole interaction. The energy transfer probability for both mechanisms is proportional to the spectral overlap of the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ emission of the $[\text{Cr}(\text{ox})_3]^{3-}$ donor and the ${}^4\text{A}_2 \rightarrow {}^2\text{T}_1$ absorption of the $[\text{Cr}(\text{bpy})_3]^{3+}$ acceptor. The spin-flip transitions of (pseudo-)octahedral Cr^{3+} are known

to shift to lower energy with increasing pressure. Because the shift rates of the two transitions in question differ, the spectral overlap between the donor emission and the acceptor absorption is a function of applied pressure. For $[\text{Rh}_{1-x}\text{Cr}_x(\text{bpy})_3][\text{NaM}_{1-y}\text{Cr}_y(\text{ox})_3]\text{ClO}_4$ the spectral overlap is thus substantially reduced on increasing pressure from 0 to 2.5 GPa. As a result, the energy transfer probability decreases with increasing pressure as evidenced by a decrease in the relative emission intensity from the $[\text{Cr}(\text{bpy})_3]^{3+}$ acceptor.

Introduction

Excitation energy transfer between a donor and an acceptor is an important photophysical process. During the past decades, it has been applied in several fields. In biochemistry, the so-called FRET, is used for analysing conformational substates of biological macromolecules and for relating their structure to the function.^[1,2] Moreover, FRET is used to follow molecular dynamics in live cells. Excitation energy transfer has been studied in conjugated organic materials in order to improve optoelectronic devices.^[3] Recently, research has become focused on solar cells, where excitation energy transfer plays a very important role for light harvesting.^[4] In all cases, investigations down to the single molecule level are needed in order to arrive at a correct description of energy transfer mechanisms in often heterogeneous and disordered environments. External pressure is a versatile tool to tune the relative energies of the different excited states of coordination compounds of transition metal ion.^[5–7] Thus Grinberg and Suchocki^[8] have recently reviewed the effect of pressure on the electronic structure of $3d^3$ transition metal ions, notably of Cr^{3+} and Mn^{4+} in oxide lattices, and Shen et al.^[9] studied the effect of external pressure on the excitation energy transfer from Cr^{3+} to Tm^{3+} co-doped into $\text{Y}_3\text{Al}_5\text{O}_{12}$. Three principal contributions to the overall energy transfer from different electronic states of Cr^{3+} were thus identified, namely from the electronic origins of the ${}^2\text{E}$ state at low temperature, from thermally activated transfer from the anti-Stokes sidebands of the ${}^2\text{E}$ state, and from the thermally activated ${}^4\text{T}_2$ state at higher temperatures.

In the Cr^{3+} co-doped three-dimensional oxalate networks of composition $[\text{Rh}_{1-x}\text{Cr}_x(\text{bpy})_3][\text{NaAl}_{1-y}\text{Cr}_y(\text{ox})_3]\text{ClO}_4$ ($\text{ox} = \text{C}_2\text{O}_4^{2-}$, $\text{bpy} = 2,2'$ -bipyridine), resonant excitation energy transfer from $[\text{Cr}(\text{ox})_3]^{3-}$ to the encapsulated $[\text{Cr}(\text{bpy})_3]^{3+}$ was observed in steady state and in time-resolved luminescence experiments, involving the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ emission of $[\text{Cr}(\text{ox})_3]^{3-}$ and the ${}^4\text{A}_2 \rightarrow {}^2\text{T}_1$

absorption of $[\text{Cr}(\text{bpy})_3]^{3+}$.^[10] At a donor doping level of $y = 1\%$ and an acceptor doping level of $x = 2.5\%$, its quantum efficiency η_{ET} was found to be 25%. Two mechanisms for this energy transfer were identified: a) A rapid process due to super-exchange coupling between $[\text{Cr}(\text{ox})_3]^{3-}$ and $[\text{Cr}(\text{bpy})_3]^{3+}$ within the first neighbour shell, with a corresponding transfer rate constant larger than 10^6 s^{-1} , contributing 70% to the total energy transfer. b) A slower process due to electric dipole–dipole interaction between $[\text{Cr}(\text{ox})_3]^{3-}$ and $[\text{Cr}(\text{bpy})_3]^{3+}$ at longer distances for those donors which have no acceptors in the nearest neighbour shell contributing the remaining 30% to the total energy transfer. The latter process follows the Förster energy transfer relation with a critical radius of approximately 11 Å. In the comparatively lightly doped systems, that is $x \leq 2.5\%$, the corresponding energy transfer rate constant was found to vary between 10^1 and 10^2 s^{-1} depending on the occupancy of the coordination shell and thus the concentration of $[\text{Cr}(\text{bpy})_3]^{3+}$ around a given $[\text{Cr}(\text{ox})_3]^{3-}$.^[10]

The probability for resonant excitation energy transfer is proportional to the spectral overlap integral between the normalised emission of the donor and the absorption of the acceptor independent on the type of interaction at the origin of the process.^[11] The exchange interaction depends upon direct overlap of the electronic wavefunctions of the donor and the acceptor and thus falls off exponentially with increasing value of R_{DA} .^[12] On the other hand, the dipole–dipole interaction is proportional to the oscillator strengths of the donor emission

[a] M. Milos, P. Pal, Prof. A. Hauser
Département de Chimie Physique
Université de Genève
30 quai Ernest-Ansermet, 1211 Geneva 4 (Switzerland)
Fax: (+41) 22 379 6103
E-mail: andreas.hauser@unige.ch

and the acceptor absorption and falls off as the inverse power of three of the donor–acceptor distance R_{DA} .^[13] For the donor–acceptor pair under consideration, the spectral overlap is provided by the sharp electronic origins of the $^2E \rightarrow ^4A_2$ spin-flip emission of $[Cr(ox)_3]^{3-}$ and the $^4A_2 \rightarrow ^2T_1$ spin-flip absorption of $[Cr(bpy)_3]^{3+}$.

Under external pressure, electronic absorption bands shift in energy. With respect to dd transitions, external pressure has two effects: the reduction in metal–ligand bond length results in an increase in ligand-field strength and a reduction in electron–electron repulsion due to an increasing electron delocalisation onto the ligands (nephelauxetic effect^[14]). For spin-allowed transitions involving the promotion of an electron from the t_{2g} to the e_g shell, the increase in ligand-field strength is dominant and spin-allowed dd transitions inevitably shift to higher energy with increasing pressure. For spin-flip transitions, that is, transitions within the same electronic configuration, the nephelauxetic effect dominates and thus these generally shift to lower energies.^[7]

In the present paper we report the shift rates for the spin-flip transitions of $[Cr(ox)_3]^{3-}$ and $[Cr(bpy)_3]^{3+}$ in high pressure experiments. As the two shift rates differ considerably, the spectral overlap between the respective donor and acceptor transitions becomes a function of external pressure, and therefore external pressure directly influences the quantum efficiency of the resonant energy transfer.

Results and Discussion

Absorption and Luminescence Spectroscopy

Mixed crystals of $[Rh_{1-x}Cr_x(bpy)_3][NaM^{III}_{1-y}Cr_y(ox)_3]ClO_4$, $M = Rh, Al$, were synthesised as described in the Experimental Section. The effective concentrations of $[Cr(bpy)_3]^{3+}$ and $[Cr(ox)_3]^{3-}$ were estimated from the concentrations of the solutions from which they were grown according to the work of von Arx et al.^[10] Thus, for the present study, the concentrations of $[Cr(bpy)_3]^{3+}$ and $[Cr(ox)_3]^{3-}$ are approximately $x = 3.5$ mole% and $y = 1$ mole%, respectively. Comparatively low doping levels are used in order to avoid energy migration within the 2E states of both $[Cr(bpy)_3]^{3+}$ and $[Cr(ox)_3]^{3-}$.^[10,15]

The corresponding neat compounds $[Cr(bpy)_3][NaAl(ox)_3]ClO_4$, $[Cr(bpy)_3][NaRh(ox)_3]ClO_4$ and $[Rh(bpy)_3][NaCr(ox)_3]ClO_4$ serve as reference compounds. Figure 1 shows the single crystal absorption spectra of the former two together with the absorption and the emission spectrum of the latter following excitation at 532 nm at 10 K in the region of the low-lying $^4A_2 \rightarrow ^2E$ and $^4A_2 \rightarrow ^2T_1$ transitions.

The absorption of $[Cr(bpy)_3]^{3+}$ includes the zero-field split R_1 and R_2 lines of the $^4A_2 \rightarrow ^2E$ transition and the structured $^4A_2 \rightarrow ^2T_1$ transition. Both are spin-flip transitions with most of the intensity in the electronic origins. For $[Cr(bpy)_3][NaAl(ox)_3]ClO_4$, the R_1 and R_2 lines are respectively at 13685.3 cm^{-1} and 13701.5 cm^{-1} and the $^4A_2 \rightarrow ^2T_1$ transition is centred at 14349 cm^{-1} with a total width of about 85 cm^{-1} (all values in air). For $[Cr(bpy)_3][NaRh(ox)_3]ClO_4$, the R_1 and R_2 lines are respectively at 13714.3 cm^{-1} and 13729.9 cm^{-1} and the $^4A_2 \rightarrow ^2T_1$

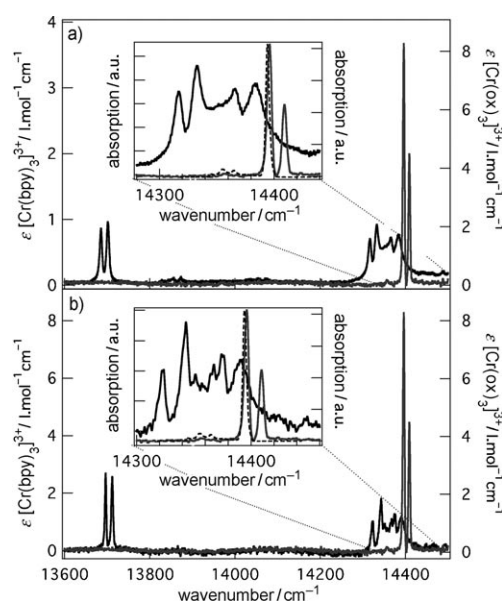


Figure 1. Single crystal absorption spectra of a) $[Cr(bpy)_3][NaAl(ox)_3]ClO_4$ and b) $[Cr(bpy)_3][NaRh(ox)_3]ClO_4$ at 10 K (black). The absorptions spectrum of $[Rh(bpy)_3][NaCr(ox)_3]ClO_4$ is included in both panels (grey). The insets show the region of the $^4A_2 \rightarrow ^2T_1$ transition of $[Cr(bpy)_3][NaM(ox)_3]ClO_4$, $M = Al, Rh$, and the $^4A_2 \rightarrow ^2E$ transition of $[Rh(bpy)_3][NaCr(ox)_3]$ on enlarged scales and include the $^2E \rightarrow ^4A_2$ luminescence of $[Rh(bpy)_3][NaCr(ox)_3]$ at 1.4 K (broken lines).

transition is centred at 14376.0 cm^{-1} . The difference in energy for corresponding transitions of around 29 cm^{-1} between the two lattices is not surprising since the chemical pressure has an important influence on the nephelauxetic effect.^[16] The ionic radius of Al^{3+} is considerably smaller than the one of Rh^{3+} .^[17] Consequently, the cavity provided by the oxalate network in which the tris-bipyridine complex is encapsulated, is smaller in the former. A smaller cavity increases the nephelauxetic effect as a result of the shorter Cr–N bond length and an increasing π -interaction between the oxalate and the bipyridine ligands.^[16] As a result, the $[Cr(bpy)_3]^{3+}$ absorptions in the cavities of $[Cr(bpy)_3][NaAl(ox)_3]ClO_4$ are shifted to lower energies compared to the $[Cr(bpy)_3][NaRh(ox)_3]ClO_4$ cavities. The absorption and emission spectrum of neat $[Rh(bpy)_3][NaCr(ox)_3]ClO_4$ consist of the spin-forbidden $^4A_2 \rightarrow ^2E$ transition, whose R_1 and R_2 lines are centred at 14396.3 cm^{-1} and 14409.0 cm^{-1} . In the emission spectrum recorded at 1.4 K included in the insets of Figure 1, the R_1 line dominates.

High-Pressure Experiments

Figure 2 shows luminescence spectra of $[Rh_{1-x}Cr_x(bpy)_3][NaM_{1-y}Cr_y(ox)_3]ClO_4$ ($M^{III} = Al^{3+}, Rh^{3+}$, $x = 0.035$, $y = 0.01$) at different pressures and at 10 K with excitation at 532 nm. The displayed spectra are normalised to the integrated intensity of the R lines of $[Cr(ox)_3]^{3-}$. Irradiation at 532 nm exclusively creates $[Cr(ox)_3]^{3-}$ in its 2E state via selective excitation into the $^4A_2 \rightarrow ^4T_2$ band followed by fast intersystem crossing.^[18] Despite this, the luminescence spectrum of the co-doped system consists of the $^2E \rightarrow ^4A_2$ emissions of both $[Cr(ox)_3]^{3-}$ and $[Cr(bpy)_3]^{3+}$ as a result of the resonant energy transfer from

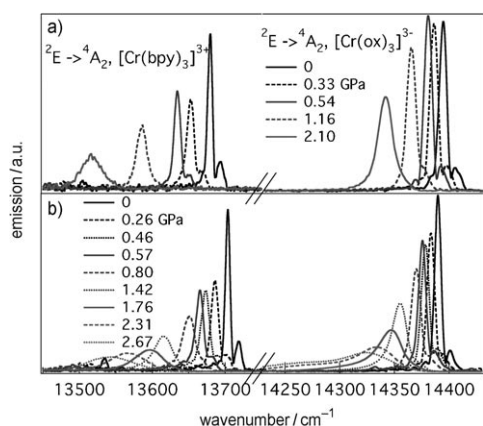


Figure 2. Luminescence spectra of $[\text{Rh}_{1-x}\text{Cr}_x(\text{bpy})_3][\text{NaM}_{1-y}\text{Cr}_y(\text{ox})_3]\text{ClO}_4$, a) $\text{M}^{\text{III}} = \text{Al}^{3+}$, b) $\text{M}^{\text{III}} = \text{Rh}^{3+}$, $x = 0.035$, $y = 0.01$ at different pressures, excitation wavelength 532 nm.

the ^2E state of $[\text{Cr}(\text{ox})_3]^{3-}$ to the $^2\text{T}_1$ state of $[\text{Cr}(\text{bpy})_3]^{3+}$ followed by rapid internal conversion. The total quantum efficiency of the energy transfer can be calculated via the relative intensity of the donor emission according to Equation (1)

$$\eta_{\text{ET}}^{\text{tot}} = \frac{I_{\text{A}}}{I_{\text{A}} + I_{\text{D}}} \quad (1)$$

In Equation (1), I_{A} and I_{D} are the integrated acceptor and donor emission intensities, and intrinsic emission quantum efficiencies of both donor and acceptor of unity are assumed at 10 K.^[13] At zero external pressure, the quantum efficiencies are 28% for $\text{M} = \text{Al}$ and 41% for $\text{M} = \text{Rh}$. These values are in line with acceptor concentrations between 3 and 4 mole%.^[10] If anything, the acceptor concentration in the Rh sample is slightly larger than in the Al sample.

With increasing pressure both the $[\text{Cr}(\text{ox})_3]^{3-}$ and the $[\text{Cr}(\text{bpy})_3]^{3+}$ emissions shift to lower energies. The pressure shift of the $[\text{Cr}(\text{ox})_3]^{3-}$ R_1 emission shown in Figure 3 has been determined previously and is $-26 \text{ cm}^{-1} \text{ GPa}^{-1}$.^[16] In the present study, the shift of this emission, precisely determined by fitting a Gaussian line shape function, serves as reference for pressure determination. Figure 3 also shows the shift of the R_1 emission of $[\text{Cr}(\text{bpy})_3]^{3+}$ as a function of pressure as determined from

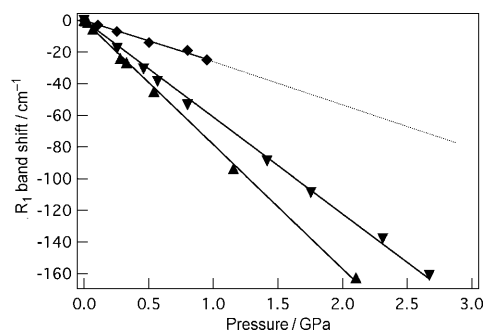


Figure 3. Shift of the luminescence of the R_1 lines of $[\text{Cr}(\text{bpy})_3]^{3+}$ in $[\text{Rh}_{1-x}\text{Cr}_x(\text{bpy})_3][\text{NaM}_{1-y}\text{Cr}_y(\text{ox})_3]\text{ClO}_4$, $\text{M} = \text{Al}$ (\circ), Rh (\blacktriangle), $x = 0.035$, $y = 0.01$ at 10 K, and of $[\text{Cr}(\text{ox})_3]^{3-}$ in $[\text{Ru}(\text{bpy})_3][\text{NaCr}(\text{ox})_3]$ (\blacktriangledown) from ref. [16].

the spectra of Figure 2. With -61 and $-79 \text{ cm}^{-1} \text{ GPa}^{-1}$ for $\text{M} = \text{Rh}$ and Al , respectively, the shift rate is 2.5 to 3 times larger than for $[\text{Cr}(\text{ox})_3]^{3-}$. This is due to the stronger π interaction of the metal t_{2g} -orbitals with the ligand π orbitals in the case of bipyridine as compared to the oxalate,^[19,20] making the nephelauxetic effect and its increase with increasing pressure stronger for the tris-bipyridine complex.

The emission spectra in Figure 2 show that with increasing pressure the R_1 lines of both species broaden to some extent. This is due to the fact that the compounds under consideration are relatively soft compared to say doped oxides such as ruby ($\text{Al}_2\text{O}_3:\text{Cr}^{3+}$)^[21,22] and thus suffer more from inhomogeneous broadening than these. In fact from this pressure induced broadening and the pressure shift, a pressure distribution of 5% around the central value can be estimated. Indeed this broadening is substantially larger than for ruby under the same conditions, but then the shift rate of $7.4 \text{ cm}^{-1} \text{ GPa}^{-1}$ for ruby is also substantially smaller.^[5]

In addition to the shifts and the broadening, the relative emission intensities of the two bands originating from the two chromophores vary as a function of pressure. This is demonstrated by Figure 4a showing the relative emission intensity of

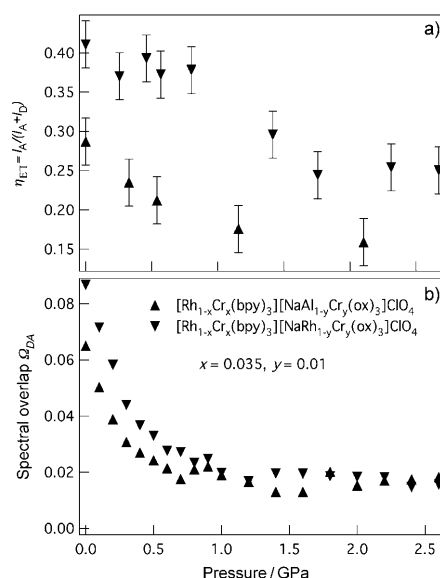


Figure 4. a) Energy-transfer quantum efficiency and b) spectral overlap between the $^2\text{E} \rightarrow ^4\text{A}_2$ emission of $[\text{Cr}(\text{ox})_3]^{3-}$ and the $^4\text{A}_2 \rightarrow ^2\text{T}_1$ absorption of spectra of $[\text{Cr}(\text{bpy})_3]^{3+}$ in $[\text{Rh}_{1-x}\text{Cr}_x(\text{bpy})_3][\text{NaM}_{1-y}\text{Cr}_y(\text{ox})_3]\text{ClO}_4$, $x = 0.035$, $y = 0.01$ as a function of pressure, $\text{M} = \text{Al}$, Rh .

the acceptor emission for both systems studied as a function of applied pressure corresponding directly to the energy transfer quantum efficiency. For both there is a net decrease in the relative intensity from the acceptor, thus it can be concluded that the quantum efficiency of the excitation energy transfer from $[\text{Cr}(\text{ox})_3]^{3-}$ to the encapsulated $[\text{Cr}(\text{bpy})_3]^{3+}$ decreases with increasing pressure.

Resonant Energy Transfer Under Pressure

As mentioned above, excitation energy transfer in the co-doped oxalate networks from $[\text{Cr}(\text{ox})_3]^{3-}$ to the encapsulated $[\text{Cr}(\text{bpy})_3]^{3+}$ is a resonant process and has two contributions: a) a fast one that is due to super-exchange coupling (Dexter mechanism^[12]) depending on the direct overlap of the electronic wavefunctions of the donor and the acceptor for those donors which happen to have an acceptor in their nearest neighbour shell, and b) a slower one that is due to the electric dipole–dipole interaction (Förster energy transfer^[23]) to acceptors at longer distances for the others.^[10] The probability for a resonant energy transfer process from the initially excited donor D^* to the acceptor A is given by Equation (2) for both types of interaction.^[24]

$$w_{\text{DA}} = \frac{2\pi}{\hbar} |\langle \text{DA}^* | H' | \text{D}^* \text{A} \rangle|^2 \Omega_{\text{DA}} \quad (2)$$

The energy transfer probability based on super-exchange coupling and dipole–dipole interaction are both proportional to the spectral overlap integral Ω_{DA} between the donor emission and the acceptor absorption, that is, the integral of the product of the normalised line shape functions of the donor emission, g_{D} , and the acceptor absorption, g_{A} , given by Equation (3).

$$\Omega_{\text{DA}} = \int g_{\text{A}}(\tilde{\nu}) g_{\text{D}}(\tilde{\nu}) d\tilde{\nu} \quad (3)$$

Whereas the emission spectra for both donor and acceptor in the co-doped system are readily available, it is not possible to measure the absorption spectra of the doped samples because of the low concentrations. In order to obtain the overlap integral according to Equation (3), hypothetical absorption spectra of the acceptor in $[\text{Rh}_{1-x}\text{Cr}_x(\text{bpy})_3][\text{NaM}^{\text{III}}(\text{ox})_3]\text{ClO}_4$ with $x=0.035$, $\text{M}=\text{Al}$, Rh are generated by shifting the absorption spectrum of the respective neat compounds $[\text{Cr}(\text{bpy})_3][\text{NaM}^{\text{III}}(\text{ox})_3]\text{ClO}_4$ so as to make their R_1 absorptions of $[\text{Cr}(\text{bpy})_3]^{3+}$ coincide with the corresponding R_1 emissions of the doped compounds. This procedure implicitly assumes that the ${}^2\text{E} \rightarrow {}^2\text{T}_1$ energy difference is roughly the same for all systems studied, an assumption, which is to some extent substantiated by the spectra of the neat compounds shown in Figure 1. We estimate a maximum error in the resulting position of the ${}^2\text{T}_1$ energy of less than 5 cm^{-1} . The resulting extrapolated spectra for the doped systems in the region of the ${}^4\text{A}_2 \rightarrow {}^2\text{T}_1$ absorption of $[\text{Cr}(\text{bpy})_3]^{3+}$ together with the experimental ${}^2\text{E} \rightarrow {}^4\text{A}_2$ emission of $[\text{Cr}(\text{ox})_3]^{3-}$ at 10 K are shown in Figure 5, both for ambient pressure and at higher pressure.

The latter assumes that the pressure shift of the ${}^4\text{A}_2 \rightarrow {}^2\text{T}_1$ transition of $[\text{Cr}(\text{bpy})_3]^{3+}$ is close to the one for the corresponding R lines. From these spectra, together with the experimentally determined shift rate of the respective R lines, the spectral overlap integral as a function of pressure shown in Figure 4b can be computed. Because of the quite different pressure shift rates of the two chromophores, the overlap inte-

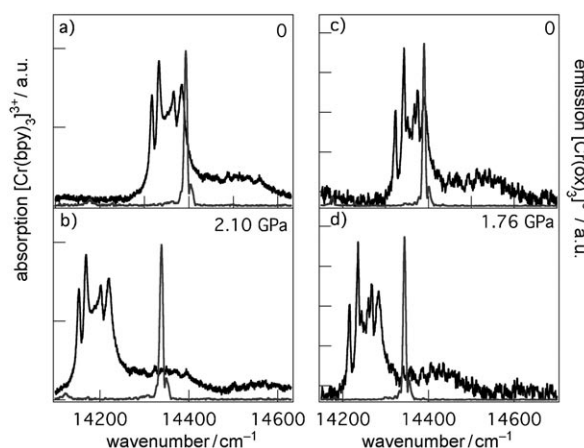


Figure 5. Extrapolated ${}^4\text{A}_2 \rightarrow {}^2\text{T}_1$ absorption of $[\text{Cr}(\text{bpy})_3]^{3+}$ (black) and experimental ${}^2\text{E} \rightarrow {}^4\text{A}_2$ emission of $[\text{Cr}(\text{ox})_3]^{3-}$ (grey) at 10 K in $[\text{Rh}_{1-x}\text{Cr}_x(\text{bpy})_3][\text{NaAl}_{1-y}\text{Cr}_y(\text{ox})_3]\text{ClO}_4$ at two different pressures, a) 0 GPa and b) 2.10 GPa and in $[\text{Rh}_{1-x}\text{Cr}_x(\text{bpy})_3][\text{NaAl}_{1-y}\text{Cr}_y(\text{ox})_3]\text{ClO}_4$ at c) 0 GPa and d) 1.76 GPa. With increasing pressure and since the shifts rates of the two transitions are not the same, the spectral overlap integral Ω_{DA} changes.

gral shows quite a strong dependence on pressure. For $\text{M}=\text{Al}$, it decreases monotonously to around 30% of its initial value at higher pressure. For $\text{M}=\text{Rh}$, the value of the overlap integral at ambient pressure is a little larger and following the same general behaviour and levelling off at the same value as for $\text{M}=\text{Al}$, which is at around 20% of the maximum value. The error introduced by the inhomogeneous broadening with increasing pressure is negligible.

Qualitatively, the decrease in the energy-transfer quantum efficiency as a function of pressure (Figure 4a) follows the decrease in the spectral overlap integral. However, this decrease is only from 28% to 16% for the Al compound and from 41% to 25% for the Rh compound. At a first glance this is far from the factors of 3 and 5 in the reduction of the overlap integral. In order to understand this, it must be remembered that the energy-transfer rate constant of the super-exchange coupling is $k_{\text{ET}}^{\text{ex}} > 10^6 \text{ s}^{-1}$, while the energy-transfer rate constant of the electric dipole–dipole interaction $k_{\text{ET}}^{\text{dd}}$ is much slower and is of the order of magnitude of the intrinsic decay rate of the donor $k_{\text{int}}^{\text{D}} = 770 \text{ s}^{-1}$. The reduction of the spectral overlap integral decreases both rate constants by the same factor, but as $k_{\text{ET}}^{\text{ex}}$ is several orders of magnitude larger than $k_{\text{int}}^{\text{D}}$, a reduction by a factor of 3 to 5 has no influence on the super-exchange contribution to the quantum efficiency as $k_{\text{ET}}^{\text{ex}}$ is still much larger than $k_{\text{int}}^{\text{D}}$. For the dipole–dipole contribution describing the energy transfer for donors with no acceptors in the nearest neighbour shell, this is different. As $k_{\text{ET}}^{\text{dd}}$ is of the order of the intrinsic decay rate constant of the donor, its decrease with decreasing spectral overlap directly results in a decrease of the dipole–dipole contribution to the energy transfer.

For the Al system, the dipole–dipole interaction contributes 30% to the total quantum efficiency,^[10] or a maximum of 9% to the experimentally determined value of 28% for the present system. The observed reduction of 12% is slightly higher but within experimental accuracy of the expected 9% for suppressing the dipole–dipole contribution.

For the Rh system, the experimentally determined total energy transfer efficiency is 41%. This is somewhat larger than for the Al system and is due to a combination of two possible sources: a) the acceptor doping level is somewhat larger than the nominal 3.5%, b) the dipole-dipole contribution at zero ambient pressure is larger than for the Al system because of the larger spectral overlap. The fact that at high pressure the energy-transfer quantum efficiency levels off at 25% indicates that indeed the acceptor concentration is somewhat higher. However, the reduction of the quantum efficiency by 16% instead of the expected 12% when taking the Al system as reference also indicates that the initial dipole-dipole contribution is higher.

Conclusions

The effect of pressure on energy transfer between [Cr(ox)₃]³⁻ and [Cr(bpy)₃]³⁺ in [Rh_{1-x}Cr_x(bpy)₃][NaM^{III}_{1-y}Cr_y(ox)₃]ClO₄, M = Rh, Al have been studied. The shift rates are -26 cm⁻¹ GPa⁻¹ for the ²E state of [Cr(ox)₃]³⁻ and -61 and -79 cm⁻¹ GPa⁻¹ for the ²T₁ state of [Cr(bpy)₃]³⁺ with M^{III} = Rh and Al, respectively. Consequently, with increasing pressure, the spectral overlap integral to which the energy-transfer probability is proportional, decreases. The energy transfer in these compounds has two contributions. The quantum efficiency of the fast contribution due to super-exchange interaction is not notably affected by the decrease of the corresponding energy-transfer rate. In contrast, for the slow contribution based on electric dipole-dipole interaction, the quantum efficiency is strongly affected by the decrease of the spectral overlap and corresponding decrease of the energy-transfer rate. The above results clearly demonstrate the power of pressure experiments in the elucidation of the mechanism of excitation energy-transfer processes between sharp line emitters and absorbers. In the present case it clearly identifies the process in question as a resonant process, rather than a phonon-assisted one. The principle can be applied to any sharp line donor-acceptor pair with direct spectral overlap, offering for instance a way to tune upconversion efficiencies in transition metal ion^[25] and co-doped lanthanide containing systems.

Experimental Section

The starting materials K₃Rh(ox)₃·4.5 H₂O, K₃Cr(ox)₃·3 H₂O, K₃Al(ox)₃·x H₂O, [Rh(bpy)₃](ClO₄)₃·3 H₂O, [Cr(bpy)₃](ClO₄)₂HbpyClO₄, and NaCl were either used as purchased or prepared according to standard procedures. The three dimensional oxalate networks with composition [Rh_{1-x}Cr_x(bpy)₃][NaM^{III}_{1-y}Cr_y(ox)₃]ClO₄ (x = 0.035, y = 0.01, M^{III} = Al³⁺, Rh³⁺) and the neat compounds [Cr(bpy)₃]-[NaM^{III}(ox)₃]ClO₄ and [Rh(bpy)₃][NaCr(ox)₃]ClO₄ were synthesised according to the general literature method of Decurtins et al.^[26] For this, stoichiometric mixtures of 10⁻² M aqueous solutions of the starting materials except for NaCl, for which the concentration was 2 × 10⁻² M, were prepared. Single crystals of the compounds in the form of perfect tetrahedra of 0.5 mm edge were obtained by slow evaporation of the solutions stored at 5 °C in a refrigerator. For the doped system, the relative volumes of the solutions to be mixed were calculated such as to obtain the desired doping concentra-

tion of Cr³⁺ complexes following von Arx et al. in such a way that 7 mole% of [Cr(bpy)₃]³⁺ and 1 mole% of [Cr(ox)₃]³⁻ in solution result in x = 0.035 and y = 0.01 in the solid.^[10]

Electronic absorption spectra were obtained on single crystals using a Fourier-transform spectrometer equipped for measuring in the infrared and visible spectral range (Bruker IFS66/S). The absorption spectra were collected at a spectral resolution of 0.5 cm⁻¹. For absorption measurements crystals were mounted on copper apertures, placed in a closed cycle cryostat (Oxford Instruments CCC1204), and collected at 10 K in an atmosphere of He exchange gas. The thickness of the crystals was measured with an optical microscope and varies from 110 μm to 285 μm depending on the sample.

Luminescence measurements were performed at 10 K using the same closed cycle cryostat and the FT spectrometer as for the absorption measurements. High pressures were achieved using a diamond anvil cell (MiniDAC of D'Anvils Ltd.). The sample chamber consisted of a hole with a diameter of 200–250 μm drilled into a pre-indented metal gasket. A small single crystal of the co-doped [Rh_{1-x}Cr_x(bpy)₃][NaM^{III}_{1-y}Cr_y(ox)₃]ClO₄ was placed in the sample chamber. The pressure was calibrated with the R₁ (⁴A₂ → ²E) transition of [Cr(ox)₃]³⁻. Silicon oil, polydimethylsiloxane trimethylsiloxyl terminated, was used as the pressure-transmitting medium. The crystals were excited at 532 nm (< 10 mW) using a DPSS LASER (ILEE VA-I-N-532) in order to selectively excite the [Cr(ox)₃]³⁻. The shift rate of the R₁ (⁴A₂ → ²E) transition of [Cr(ox)₃]³⁻ was determined previously at -26 cm⁻¹ GPa⁻¹. The exact position of the R₁ luminescence band of [Cr(ox)₃]³⁻ was determined with a Gaussian fit, and using the above shift rate, the pressure within the DAC was established for each experiment.

Acknowledgements

The authors thank the Swiss National Science Foundation (grant number 200020-125175) for funding, and N. Amstutz for her help in the preparation of the samples.

Keywords: [Cr(bpy)₃]³⁺ · [Cr(ox)₃]³⁻ · 3D oxalate networks · excitation energy transfer · high pressures

- [1] E. A. Bykova, J. Zheng, *Spectra FRET: A Fluorescence Resonance Energy Transfer Method in Live Cells*, Springer, New York, **2007**.
- [2] B. Ananthanarayanan, Q. Ni, J. Zhang in *Biophysical Tools for Biologists, Vol. 2: In Vivo Techniques* [Eds.: J. J. Correia, W. Dettrich], *Methods in Cell Biology*, Academic Press, Elsevier, San Diego, USA, **2008**, 89, pp. 37–57.
- [3] F. Laquai, Y. S. Park, J. J. Kim, T. Basche, *Macromol. Rapid Commun.* **2009**, 30, 1203–1231.
- [4] M. Grätzel, *Nature* **2001**, 414, 338–344.
- [5] J. K. Grey, I. S. Butler, *Coord. Chem. Rev.* **2001**, 219, 713–759.
- [6] H. G. Drickamer, C. W. Frank, *Electronic Transitions and the High Pressure Chemistry and Physics of Solids*, Chapman and Hall, New York, **1973**.
- [7] K. L. Bray, *Top. Curr. Chem.* **2001**, 213, 1–94.
- [8] M. Grinberg, A. Suchocki, *J. Lumin.* **2007**, 125, 97–103.
- [9] Y. R. Shen, T. Riedener, K. L. Bray, *Phys. Rev. B* **2000**, 61, 11460–11471.
- [10] V. S. Langford, M. E. von Arx, A. Hauser, *J. Phys. Chem. A* **1999**, 103, 7161–7169.
- [11] E. I. Solomon, A. B. P. Lever, *Inorganic Electronic Structure and Spectroscopy*, Wiley, New York, **1999**.
- [12] D. L. Dexter, *J. Chem. Phys.* **1953**, 21, 836–850.
- [13] A. Hauser, M. E. von Arx, V. S. Langford, U. Oetliker, S. Kairouani, A. Pilonnet, *Top. Curr. Chem.* **2004**, 241, 65–96.
- [14] C. K. Jørgensen, *Discuss. Faraday Soc.* **1958**, 110–115.

- [15] M. Milos, S. Kairouani, S. Rabaste, A. Hauser, *Coord. Chem. Rev.* **2008**, 252, 2540–2551.
- [16] M. Milos, A. Hauser, *Inorg. Chem.* **2010**, 49, 3402–3408.
- [17] J. E. Huheey, A. E. Keiter, R. L. Keiter, *Chimie Inorganique*, De Boeck Université, **1996**.
- [18] M. E. von Arx, V. S. Langford, U. Oetliker, A. Hauser, *J. Phys. Chem. A* **2002**, 106, 7099–7105.
- [19] M. Atanasov, T. Schönherr, *Inorg. Chem.* **1990**, 29, 4545–4550.
- [20] M. A. Atanasov, T. Schönherr, H. H. Schmidtke, *Theor. Chim. Acta* **1987**, 71, 59–73.
- [21] K. Nakano, Y. Akahama, Y. Ohishi, H. Kawamura, *Jpn. J. Appl. Phys. Part 1* **2000**, 39, 1249–1251.
- [22] K. Syassen, *High Pressure Res.* **2008**, 28, 75–126.
- [23] T. Förster, *Ann. Phys.* **1948**, 437, 55–75.
- [24] B. Henderson, G. F. Imbusch, *Optical Spectroscopy of Inorganic Solids*, Clarendon Press, Oxford, **1989**.
- [25] O. S. Wenger, G. M. Salley, H. U. Güdel, *J. Phys. Chem. B* **2002**, 106, 10082–10088.
- [26] S. Decurtins, H. W. Schmalle, R. Pellaux, P. Schneuwly, A. Hauser, *Inorg. Chem.* **1996**, 35, 1451–1460.

Received: April 21, 2010

Published online on August 16, 2010