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Time-resolved chiroptical luminescence spectra of $UO_2{}^{2+}$ in cubic $Na[UO_2(CH_3COO)_3]$ crystals: evidence for circular dichroic self-absorption

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Abstract

Time-resolved chiroptical luminescence (TR-CL) measurements are reported for cubic crystals of $Na[UO_2(CH_3COO)_3]$. These crystals belong to the enantiomorphic space group $P2_13$, and they exhibit strong chiroptical activity within the $\Sigma_g^+ \leftarrow \Pi_g$ emission spectrum of $UO_2{}^{2+}$. Circular polarization is observed in the origin line of this spectrum, as well as in a vibronic progression from the origin based on the symmetric stretching mode (ν_s) of UO_2^{2+}. The TR-CL results are used to confirm the presence of circular dichroic self-absorption within the origin transition.

1. Introduction

Sodium uranyl acetate, $Na[UO_2(CH_3COO)_3]$, spontaneously resolves upon crystallization into enantiomorphic crystals of the cubic space group $P2_13$ [1]. Spectroscopically, these crystals are of interest because they exhibit strong chiroptical activity in their absorption and emission spectra. The lowest-energy absorption band is assigned to an electronic transition, $\Sigma_g^+ \rightarrow \Pi_g$, localized on the UO_2^{2+} ions. In unpolarized absorption measurements, this band shows many vibronic components based on a common origin line. However, in circularly polarized absorption measurements, only the origin and one subset of vibronic lines exhibit circular dichroic properties. The vibronic lines belonging to a progression in the symmetric stretching mode (ν_s) of UO_2^{2+} show strong circular dichroism, but the remaining vibronic lines do not exhibit circular dichroic properties. An explanation for these observations has been given in previous work [2].

The luminescence spectrum of $Na[UO_2(CH_3COO)_3]$ can be assigned entirely to origin and vibronic lines associated with the $\Sigma_g^+ \leftarrow \Pi_g$ electronic transition of UO_2^{2+}. At cryogenic temperatures, the luminescence spectrum shows many sharp lines, a subset of which exhibit extraordinarily strong chiroptical activity (circularly polarized luminescence, or CPL). The latter are assigned to the origin transition and to vibronic transitions associated with a progression in the symmetric stretching mode of UO_2^{2+}. The other vibronic transitions show no chiroptical activity. Also evident from the emission (and excitation) spectra are several defect (or minor) UO_2^{2+} sites within the crystal, and energy transfer between the sites has been of interest to several research groups [3–5].

In a recent study, we examined the steady-state chiroptical luminescence properties of $Na[UO_2(CH_3COO)_3]$, and analyzed the results within the context of vibronic optical activity theory [6]. In the course of that study, we noticed a number of interesting features associated with luminescence in the $\Sigma_g^+ \leftarrow \Pi_g$ transition origin region. The lineshape and intensity of the zero-phonon (origin) transition (as compared to other members of the symmetric progression) are indicative of self-absorption in this region. The appearance of the circularly polarized luminescence (CPL) lineshape is even more striking, as it appears as a band of similar linewidth to the TL lineshape, but with a sharp and deep "hole" apparent within the line. (The transition origin region is shown in the inset of Fig. 1.)

The unusual lineshape of CPL in the transition origin region has been attributed to circular dichroic self-absorption [6]. In this paper, we provide further evidence supporting this proposal, namely, time-resolved chiroptical luminescence (TR-CL) measurements made within the transition origin region. These measurements clearly point to a mechanism consisting of multiple emission-reabsorption events occurring within the crystal, leading to diffusion of excitation energy through the crystal. Furthermore, the polarization state of the emitted photons helps to determine their fate: whether

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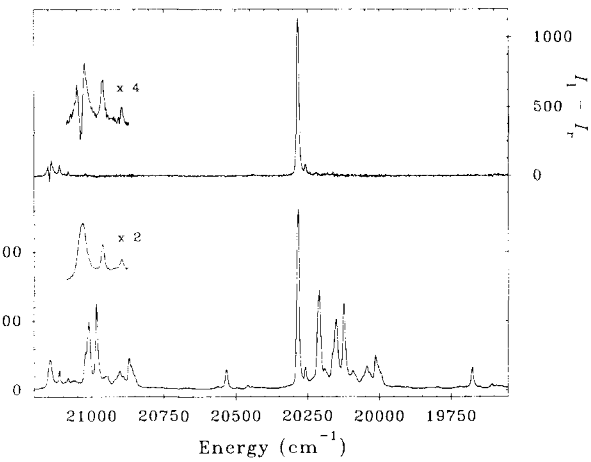

Fig. 1. CPL (top trace, $I_l - I_r$) and TL (bottom trace, $I_l + I_r$) spectra for a single crystal of Na[UO$_2$(CH$_3$COO)$_3$] at 15 K. This spectral region covers the origin and first member of the vibronic progression in the symmetric UO$_2^{2+}$ stretch. The inset shows the transition origin region from 21 170 to 21 070 cm^{-1}. The crystal was excited with continuous radiation at 457.9 nm (argon ion laser) and the spectral resolution was 1 cm^{-1}.

they are reabsorbed by the crystal or are able to escape to our instrumental detector.

2. Results and discussion

Time-resolved chiroptical luminescence results obtained at an emission wavelength corresponding to the bottom of the "dip" in the transition origin region are displayed in Fig. 2. These results were obtained from a relatively large crystal, measuring *ca.* 3 mm thick, under conditions where the emission was collected at 180° with respect to the excitation direction. The time-resolved total luminescence data ($I_l + I_r$, where I_l and I_r correspond to intensities of left- and right-circularly polarized light) are poorly fit by a single exponential decay function and are only reasonably well fit by a sum of three exponentials, with decay constants of 7140, 1330 and 714 s^{-1}. (Recall that large decay constants reflect faster decay components and small decay constants reflect slower decay components.) The time-resolved circularly polarized luminescence data ($I_l - I_r$) are also reasonably fit by the sum of three exponentials: two negative exponentials with relatively large decay constants (9170 and 1960 s^{-1}) and one positive exponential with a smaller decay constant (640 s^{-1}). As is evident from the figure, the emission at this energy is right-circularly polarized at times close to that of the excitation pulse and then becomes left-circularly polarized at longer times. The multi-exponential nature of the observed decays (both TL and CPL) is due to multiple emission-reabsorption events taking place in the crystal, and the sign inversion apparent in the time-resolved CPL is due to the preferential reabsorption of left-circularly polarized photons during the course of emission.

A schematic depiction of excitation energy migration through a Na[UO$_2$(CH$_3$COO)$_3$] crystal is shown in Fig. 3. Each dot, in the figure represents a UO$_2^{2+}$ ion undergoing a zero-phonon (origin) emissive transition. Conditions close to the time of excitation are shown in the top frame, and conditions at subsequent times are shown in the next two frames. We assume that

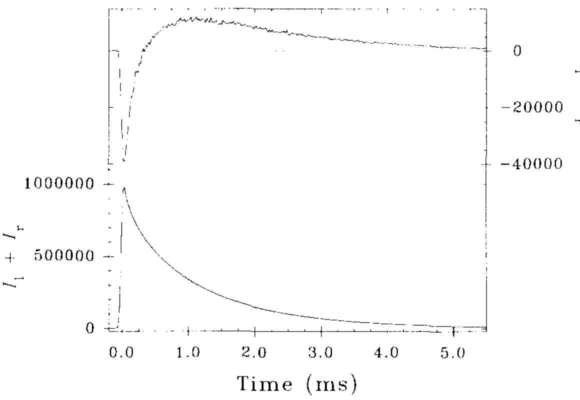

Fig. 2. Time-resolved CPL (top trace, $I_l - I_r$) and TL (bottom trace, $I_l + I_r$) for a single crystal of Na[UO$_2$(CH$_3$COO)$_3$] recorded at the "dip" in the CPL of the origin transition region (21 140 cm^{-1}). The crystal temperature was 15 K and the emission was excited with chopped radiation at 457.9 nm (argon ion laser). The emission resolution was 2 cm^{-1}.

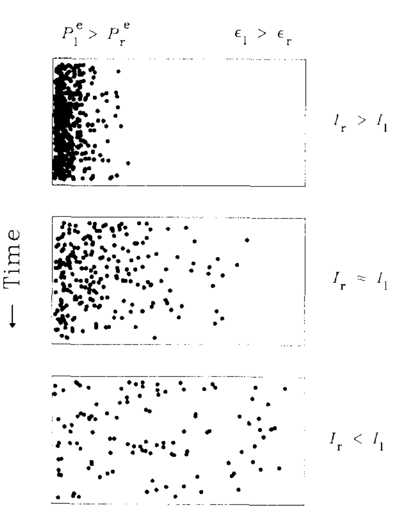

Fig. 3. Schematic representation of energy migration within a single crystal of Na[UO$_2$(CH$_3$COO)$_3$]. Excitation is from the left side of the figure and emission detection is on the right. P_l^e and P_r^e denote the probabilities of emission of left and right circularly polarized photons by excited UO$_2^{2+}$ ions, and ϵ_l and ϵ_r denote the absorptivities of left and right circularly polarized light by ground-state UO$_2^{2+}$ ions. I_l and I_r denote the experimentally detected intensities of left and right circularly polarized emission. We assume an exponential distribution of excited UO$_2^{2+}$ ions through the crystal. The evolution of this distribution is shown as a function of time from the top frame to the bottom frame of the figure.

excitation is from the left side of the figure and that detection of emitted radiation occurs on the right side of the figure. We further assume that the crystal exhibits strong left-circularly polarized luminescence in its origin transition.

Upon initial excitation, the majority of emitting UO_2^{2+} ions are located towards the excitation side of the crystal. Emission from these ions will be strongly (but not purely) left-circularly polarized. (Recall that we are depicting only those ions that are undergoing a zero-phonon $\Sigma_g^+ \leftarrow \Pi_g$ transition.) Any ground-state UO_2^{2+} ion can reabsorb the emitted photons, and the absorbing transition will be the zero-phonon $\Sigma_g^+ \rightarrow \Pi_g$ transition. This transition is strongly circular dichroic, and photons of the same (left) handedness as those emitted by the initially excited UO_2^{2+} ions will be preferentially absorbed. Photons of opposite (right) handedness will have a smaller probability of being reabsorbed. Thus, photons that make it through the crystal to the instrument detector are likely to have right circular polarization.

As the emission-reabsorption events take place, the excitation energy will effectively migrate through the crystal, towards the detector side of the crystal. As this occurs, the probability of a left-circularly polarized photon being reabsorbed by the crystal will decrease since the absorption pathlength will decrease. Thus, the polarization of the detected radiation will become more left-circularly polarized as the energy migration occurs. This process is illustrated in the second and third frames of Fig. 3.

The above, qualitative model of radiative transport modulated by emission polarization can be used to explain both the emission spectral lineshapes within the transition origin region shown in Fig. 1 and the time-resolved results shown in Fig. 2. Furthermore, there are a number of experimental consequences predicted by the model. The degree of reabsorption will be dependent on crystal size, as well as excitation-emission geometry and excitation characteristics (*i.e.* continuous or pulsed excitation, excitation power and excitation wavelength). All of these factors have been shown to cause major changes in the transition origin region, leading to difficulties in the reproduction of results obtained through this region. As an example of the effects of crystal size on lifetime measurements, emission decay rates measured on a small crystal (*ca.* 0.5 mm thick) under similar experimental conditions as for the results presented above give decay constants $>2580\ s^{-1}$, reflecting faster decay processes. We note that TL lifetime measurements made at any emission wavelength will be similarly affected by changes in experimental setup, while polarization and spectral bandshape differences will only be observed in the transition origin region.

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