Two-Photon Spectroscopy of d^3 Transition Metals: Near-IR-to-Visible Upconversion Luminescence by Re^{4+} and Mo^{3+}

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The design and characterization of new materials capable of converting low-energy photon input into discrete higher-energy luminescence (i.e. upconversion (UC)) plays an important role in the field of materials-related inorganic chemistry. Such materials have already found use, for example, as coherent laser light sources,[1] 3-D imaging materials,[2] or enhanced IR quantum counters.[3] The majority of this research has been devoted to the study of rare-earth (RE) ions due to their ability to luminesce from multiple excited states. Several d^2, d^3, d^4, and d^8 transition-metal (TM) ions also luminesce from more than one excited state, but these ions have received little attention as potential UC materials.[4] We are now exploring the multiphoton properties of these ions in various chemical environments, with particular focus on comparison to the analogous properties of the RE ions. In this communication we describe the first photon UC results for any d^3 TM ions reported to date, namely Re^{4+} and Mo^{3+}. Despite their similar electronic structure, UC in these two ions is found to proceed via fundamentally different mechanisms, reflecting the role of spin selection rules in excited-state energy transfer (ET). The need to consider spin as a viable quantum number in TM ions constitutes an important difference between TM and RE ions in relation to UC processes. The observation of intense Re^{4+} UC even at room temperature represents a significant development in the study of this new class of photon UC materials.

Figure 1 presents a generalized energy-level diagram for octahedral d^3 ions.[5] The series of doublet excited states derived from intraconfigurational ("spin flip") electronic excitations in both Re^{4+} and Mo^{3+} have been studied extensively by absorption (Abs) and luminescence spectroscopies,[6] where the most striking observation was that of luminescence from both the first ($^2T_1$, ^2E, near-IR) and second ($^2T_2$, red) excited-state multiplets. In Mo^{3+}, excitation into the higher-energy, broader, and more intense $^4T_2$ and $^4T_1$ interconfigurational transitions leads to rapid relaxation followed by intense red luminescence (down arrow in Figure 1). We have studied samples of $ReCl_6^{2-}$ in Cs_2ZrCl_6 and MoX_6^{3-} in Cs_2NaYX_6 (X=Cl, Br) and observe red luminescence in both samples upon excitation in the near-IR, well below the energies of the luminescent excited states.[7]

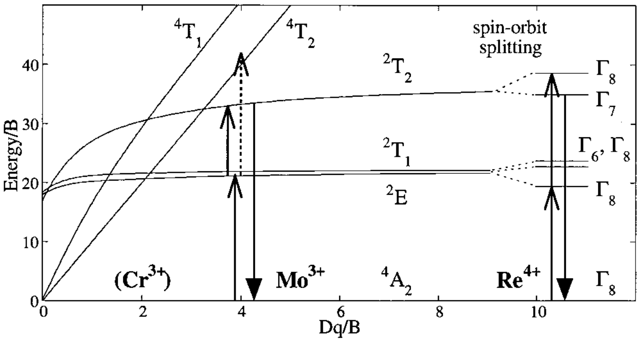

Figure 1. d^3 Tanabe-Sugano energy-level diagram (using parameters from Mo^{3+}: $C/B = 3.7$, $B = 487^{5,6a}$). Up arrows indicate two-photon processes observed in Mo^{3+} and Re^{4+}. Down arrows indicate luminescence used to monitor these processes.

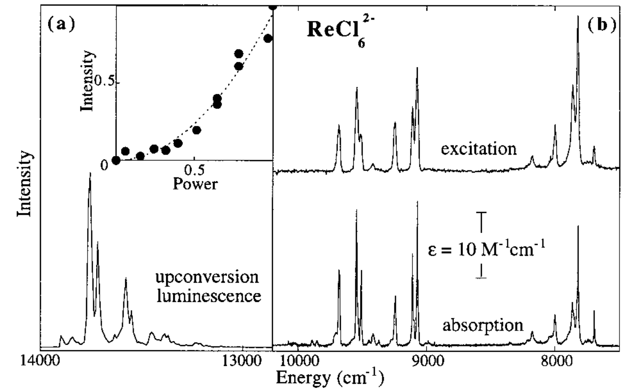

Figure 2. (a) 15 K UC luminescence of 2.5% Re^{4+}:Cs_2ZrCl_6. Inset: UC intensity as a function of near-IR excitation power. The curve shows predicted two-photon behavior. (b) 15 K near-IR UC excitation scan. 10 K near-IR absorption. Note the discontinuous energy axis.

Figure 2 presents (a) the 15 K UC luminescence spectrum of $ReCl_6^{2-}$ and (b) the 15 K near-IR excitation scan obtained when monitoring this luminescence, compared with the 10 K near-IR Abs spectrum. Power-dependence measurements (Figure 2a, inset) reveal the participation of two near-IR excitation photons for each red photon emitted, as expected from Figure 1. From Figure 2b, UC excitation scans closely follow the Abs profile, even in the higher-energy ($\Gamma_6(^2T_1)$, $\Gamma_8(^2E)$) region where no excited-state Abs (ESA) at the same photon energy can occur. This observation allows the conclusion that the dominant mechanism for UC in Re^{4+} under these conditions involves ET between two ions in the excited $\Gamma_8(^2T_1)$ state to generate one ion in the ground $\Gamma_8(^4A_2)$ state and one in the doubly excited $\Gamma_8(^2T_2)$ state, which subsequently relaxes to $\Gamma_7(^2T_2)$ and luminesces (Figure 1). Time-dependent measurements confirm the existence of an efficient ETUC mechanism that persists up to room temperature.[8]

Red luminescence is also observed in Mo^{3+} with broadband near-IR excitation (Figure 3a). The quadratic power dependence (Figure 3a, inset) confirms that this luminescence derives from UC. Although the distribution of excited states in Mo^{3+} (Figure 1) results in favorable resonance of a first ($^4A_2 \rightarrow {}^2T_1$, ^2E) and second ($^2T_1$, $^2E \rightarrow {}^4T_2$) excitation step, resulting in a plausible one-color UC pathway, one-color excitation (Figure 3b) fails to yield any observable UC luminescence. Comparison to a Re^{4+}

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(1) Lenth, W.; Macfarlane, R. M. *Opt. Photonics News* **1992**, *3*, 8.

(2) Downing, E.; Hesselink, L.; Ralston, J.; Macfarlane, R. *Science* **1996**, *273*, 1185.

(3) Chivian, J. S.; Case, W. E.; Eden, D. D. *Appl. Phys. Lett.* **1979**, *35*, 124.

(4) (a) Wermuth, M.; Güdel, H. U. *Chem. Phys. Lett.* **1998**, *281*, 81. (b) Jacobsen, S. M.; Güdel, H. U. *J. Lumin.* **1989**, *43*, 125. (c) May, P. S.; Güdel, H. U. *J. Chem. Phys.* **1991**, *95*, 6343. (d) Oetliker, U.; Riley, M. J.; May, P. S.; Güdel, H. U. *Coord. Chem. Rev.* **1991**, *111*, 125 and references therein.

(5) Tanabe, Y.; Sugano, S. *J. Phys. Soc. Jpn.* **1954**, *9*, 753, 766.

(6) See for example: (a) Stranger, R.; Moran, G.; Krausz, E.; Güdel, H.; Furer, N. *Mol. Phys.* **1990**, *69*, 11, (b) Flint, C. D.; Paulusz, A. G. *Mol. Phys.* **1981**, *44*, 925, (c) Flint, C. D.; Paulusz, A. G. *Mol. Phys.* **1981**, *43*, 321 and references therein.

(7) 2.5% TM doped Cs_2ZrCl_6 and Cs_2NaYX_6 (X = Cl, Br) samples were synthesized at 820 °C from stoichiometric mixtures of CsX, ZrX_4, NaX, YX_3, Cs_2ReCl_6 and/or MoX_3, and single crystals were grown from the melts by the Bridgman technique. All samples and precursors were handled under inert N_2 and He atmospheres only. Abs spectra were collected on a Cary 5e spectrometer with closed-cycle cryogenic cooling. All luminescence and excitation spectra were excited with a 100 W halogen lamp, dispersed through a 3/4 m single monochromator (Spex 1702), and detected by a PMT (RCA C31034). Typical powers in excitation scans were 4 $\mu W/mm^2$. Sample cooling was achieved with a quartz He flow tube. Second color excitation involved direct output from a 100 W halogen lamp and a 1.65 μ Ge cutoff filter.

(8) Gamelin, D. R.; Güdel, H. U. To be submitted for publication.

10.1021/ja982742m CCC: $15.00

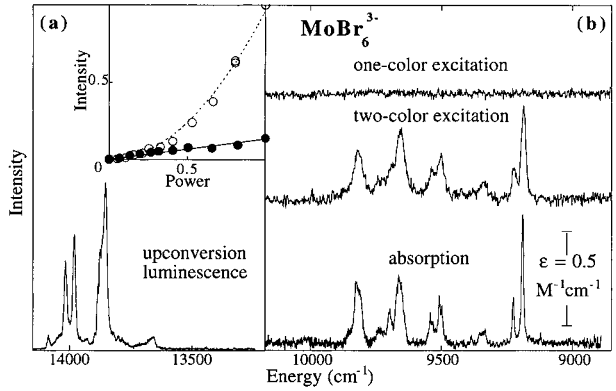

Figure 3. (a) 15 K UC luminescence of 2.5% Mo^{3+}:Cs_2NaYBr_6. Inset: UC intensity as a function of (○) total near-IR power and (●) 9065 cm^{-1} power for fixed second-color power, normalized at low powers. Curves show predicted two-photon (---) and one-photon (—) behavior. (b) 15 K near-IR UC excitation scans with one-color (top) and with addition of a second color ($E_2 \leq 6060$ cm^{-1}) (middle). 10 K near-IR absorption. Similar results are observed for 2.5% Mo^{3+}:Cs_2NaYCl_6. Note the discontinuous energy axis.

sample of the same concentration under the same conditions yields an experimental upper limit of ca. 10^{-3} relative UC efficiency in the Mo^{3+} sample. Mo^{3+} UC luminescence is, however, observed in a two-color experiment (Figure 3b) in which the first color scans through the lowest excited states while the sample is illuminated with a second color of lower energy, resonant only with the intraconfigurational ESA transitions $^2T_1$, $^2E \rightarrow {}^2T_2$ (Figure 1). The observed power dependence under these conditions (Figure 3a, inset) is linear in each color, indicating an ESA mechanism. The dominant UC mechanism in Mo^{3+} is therefore two-color ESA, not one-color ETUC as in Re^{4+}, despite favorable energetic resonance conditions for a one-color mechanism.

To understand the contrasting results described above, the ETUC rates predicted for these two ions are compared. Because energy gaps are large in all cases ($\Delta/h\nu_{max} \geq 12$ for $^2T_2-{}^2T_1/{}^2E$ and $^2T_1/{}^2E-{}^4A_2$ gaps in both ions), 15 K multiphonon relaxation is assumed negligible. Furthermore, in the absence of upconversion, the steady-state populations of the intermediate excited states in the two samples are comparable despite their different Abs oscillator strengths, due to the inverse relationship between oscillator strength and lifetime. The relative one-color UC luminescence intensities, I_{UC}, can therefore be directly related to the relative ETUC rates obtained from eq 1, which describes ET

$$W_{ET} = \frac{(\text{constant})}{\nu^2 n^4 R^6} f_D f_A \int g_D(\nu) g_A(\nu)\, d\nu \qquad (1)$$

rates for resonant dipole−dipole donor−acceptor (DA) interactions[9] (ν is the average frequency of the resonant electronic transition, n is the index of refraction, R is the DA separation, f is the oscillator strength, and the integral represents the DA spectral overlap factor for normalized Abs and emission intensities). The magnitudes of the various terms are evaluated by using the Abs and luminescence spectra of these species,[10] and the greatest differences are found to derive from the oscillator strengths f_D and f_A: Although spin-forbidden in both ions, f_D is ca. 10^2 times larger in Re^{4+} than in Mo^{3+} due to the 4-fold greater SO coupling in Re^{4+}, as this relaxes the spin selection rules for Abs (see ϵ values in Figures 2 and 3). f_A is estimated[10] to be ca. 10^3 times larger in Re^{4+}, where it relates to a spin-allowed doublet-to-doublet transition, than in Mo^{3+}, where it relates to a spin-forbidden doublet-to-quartet transition. The ratio of ETUC intensities is therefore estimated to be $I_{Mo}/I_{Re} \approx 10^{-5}$, despite a DA spectral overlap integral that is approximately three times larger in Mo^{3+} than in Re^{4+}. This is consistent with the experimental upper limit for one-color excitation of $I_{Mo}/I_{Re} \leq 10^{-3}$. Introduction of a second color in Mo^{3+} excitation partially bypasses the spin restrictions of eq 1 by introducing direct doublet-to-doublet ESA, and renders the UC observable (Figure 2b).

In summary, UC luminescence has been observed in d^3 TM ions for the first time. Mo^{3+} and Re^{4+} show dramatically different properties that can be related to differences in oscillator strengths due to spin selection rules. The observation of an energetically resonant but spin-blocked UC pathway in Mo^{3+} contrasts what is observed in RE UC materials, where SO coupling is significantly greater due to contraction and high shielding of the f orbitals, and consequently energy resonance conditions dominate over spin selection rules. The observation of UC luminescence in Mo^{3+} and Re^{4+} reveals an opportunity to study new phenomena in TM photophysics, and the spectroscopic comparison of their UC properties presented here provides direction for future work in this area. Further advances in the design and characterization of TM systems as potential new UC materials appear promising.

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(9) Di Bartolo, B. *Optical Interactions in Solids*; Wiley: New York, 1968; Chapter 18. Higher order electric-multipole or magnetic-dipole/multipole contributions are neglected since the dipole−dipole term described by eq 1 is expected to dominate.

(10) The ratio $(f_D)_{Mo}/(f_D)_{Re} = 0.015$ is determined experimentally from Figures 2 and 3. Values for $(f_A)_{Mo}$ and $(f_A)_{Re}$ are estimated from observed spin-forbidden, laporte-forbidden ($^4A_2 \rightarrow {}^2E$, $f = 6 \times 10^{-8}$) and spin-allowed, laporte-forbidden ($^4A_2 \rightarrow {}^4T_2$, $f = 8 \times 10^{-5}$) transitions of $MoBr_6^{3-}$, respectively, and yield a ratio of $(f_A)_{Mo}/(f_A)_{Re} \approx 10^{-3}$. For the spectral overlap integral we assume that $g_A(\nu)$ is similar in ground- and excited-state absorption, justified by the fact that the intermediate excited state has the same electronic configuration and geometry as the ground state. We assume equal refractive indices for the two crystals. The ratio $(R^{-6})_{Mo}/(R^{-6})_{Re} = 0.6$ is calculated from crystallographic parameters.