

Near infrared absorption and luminescence spectroscopy as a probe to the low-energy excited states of organometallics and inorganic materials

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Introduction

Transition metal compounds offer an exceptionally rich electronic structure with a variety of different electronic states in the visible and near infrared (NIR) spectral regions.^{1,2} The NIR is of particular interest because the lowest excited electronic state is often found in this domain. Important technological applications of solids containing transition metal ions include tunable laser materials.³ We present in the following an overview of the applications of NIR spectroscopy to transition metal compounds, illustrating some of the key phenomena determining their properties. NIR spectroscopy leads to a detailed quantitative characterization of the excited states and vibronic dynamics of these materials and important new insight into their photophysics and photochemistry.

Experimental

For all spectroscopic investigations the samples were placed in a helium gas, continuous-flow cryostat (Oxford Instruments CF 1204) with quartz windows. The temperature of the sample was determined by means of a Rh-Fe resistor on the sample holder.

The excitation source was a 150 W Xe arc lamp (ICL LX-150UV) filtered through a 10 cm cell with quartz windows containing a copper sulfate solution. The UV excitation was passed through a Schott UG11 color filter and focused onto the sample using quartz lenses. A spherical mirror served to collect the luminescence perpendicular to the excitation and to focus it onto the entrance slit of a monochromator (Spex 1800-II or Spex 500M). A long-pass filter was placed in front of the entrance slit of the monochromator. A number of gratings blazed at 500 nm, 1000 nm and 1600 nm were used for the experiments presented in this work. The luminescence was detected with a Ge detector (ADC 403L or ADC 403UL) or a photomultiplier (Hamamatsu R406) and a lock-in amplifier (Stanford Research SR510). The data acquisition was controlled by a personal computer using software written in our laboratory and the MS-DOS operating system. Absorption spectra were measured with a Varian Cary 5E spectrometer.

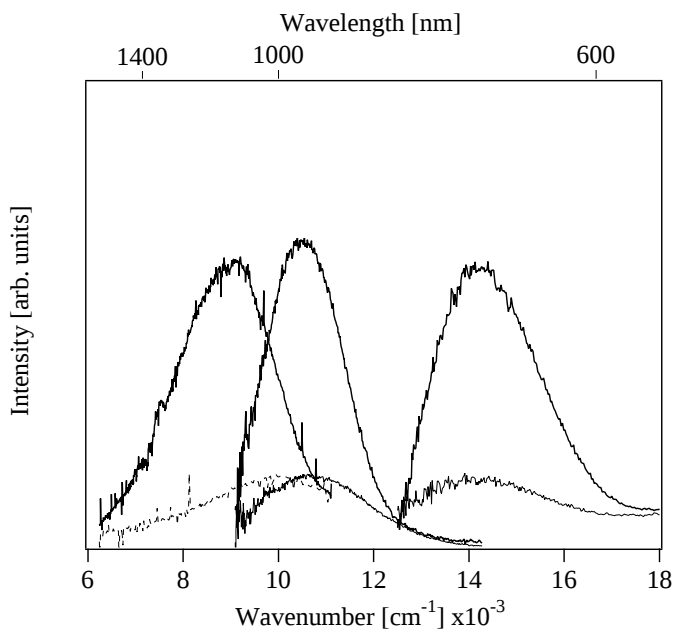


Figure 1. NIR luminescence spectra of three organorhenium compounds at 10–20 K (solid lines) and at 100–120 K (dotted lines).

Near infrared luminescence spectroscopy of organorhenium compounds

Many organometallic compounds prepared during the last decade show NIR luminescence, an aspect of their physical properties that has not received much attention.⁴ We have studied the luminescence spectra of a series of low-coordinate organorhenium molecules and have discovered an astonishing variation of the luminescence wavelength.⁵ Three examples of such systems are shown in Figure 1. The large bandwidths and Stokes shifts indicate considerable structural changes between the molecular ground and emitting electronic states, important determinants for the photochemical properties of these compounds.

Resolved vibronic structure of tetrachloro- and tetrabromopalladate

The luminescence properties of Pd(II) in the solid state are of interest because of the d^8 electron configuration it shares with Ni(II) and Pt(II), ions for which laser action has been demonstrated in the solid state.³ We have found luminescence in the NIR from K_2PdCl_4 and K_2PdBr_4 . The spectra are shown in Figure 2 and Figure 3, respectively. We observe resolved vibronic structure with separations of the peaks corresponding to ground state vibrational frequencies known from Raman measurements.⁶ The intensity distribution within the progressions is calculated using time-dependent quantum mechanics^{7,8} and leads to Pd–X bond length changes in the emitting state of 0.11 Å and 0.09 Å for the chloride and bromide, respectively. Currently, we are examining multi-mode models to account for the resolved fine structure on each member of the vibronic progression in K_2PdBr_4 . The parameters used in the calculations are summarized in Table 1. It is interesting to

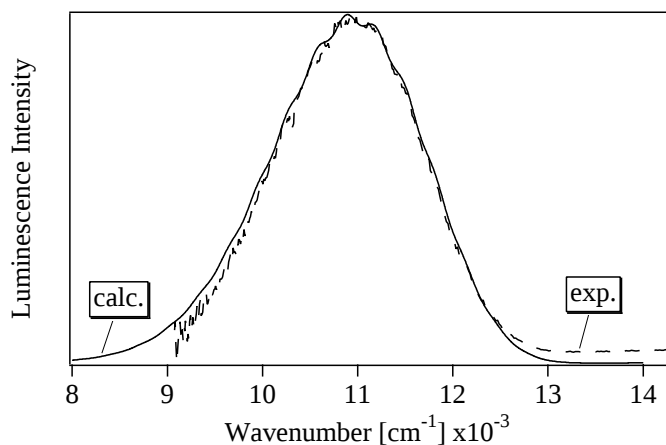


Figure 2. Experimental (dotted line) and calculated (solid line) luminescence spectra of K_2PdCl_4 .

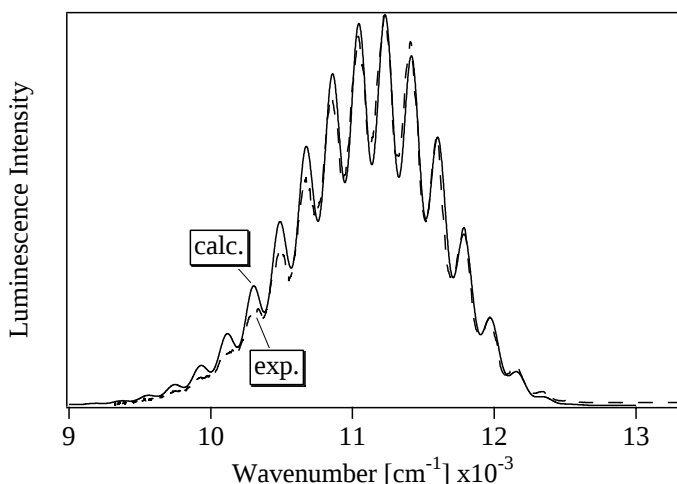


Figure 3. Experimental (dotted line) and calculated (solid line) luminescence spectra of K_2PdBr_4 .

note that neither of the two compounds show evidence for a large energy gap between the absorption and emission spectra, as was observed for K_2PtCl_4 .⁹

Intervalence charge transfer bands

Bimetallic complexes containing transition metal ions in different oxidation states often show a characteristic charge-transfer band in the NIR caused by the transfer of an electron between the two metal centers. The band shapes of these transitions are highly asymmetric, an example is shown in Figure 4. Time dependent quantum mechanical models can be adapted to these

Table 1. Parameters used for the calculated luminescence spectra in Figures 2 and 3.

	K ₂ PdCl ₄	K ₂ PdBr ₄
Electronic origin (cm ⁻¹)	13,000	12,530
hν _{alg} (cm ⁻¹)	303.6	187.4
Huang–Rhys parameter S	7.60	7.85
Emitting state distortion δr _{Pd-X} (Å)	0.11	0.09
Width of vibronic transitions T (cm ⁻¹)	42	108

two-chromophore systems and reproduce the asymmetric bandshapes.^{10–12} The calculation shows considerable coupling between the two limiting forms of the systems at the physical origin of the asymmetric band shape, even for the “valence-trapped” system¹³ investigated in our work. Detailed information on this simple category of electron-transfer processes can be obtained from the spectra.

NIR characterization of NaCoC₆₀•3THF

The coordination of transition metals to Buckminsterfullerenes has attracted much interest in recent years. In Figure 5, the NIR luminescence of NaCoC₆₀•3THF is depicted. The first band is located at 730 nm. Two vibrational sidebands at 815 and 915 nm can be distinguished. The comparison with the corresponding C₆₀ NIR luminescence^{14,15} shows that the coordination to Co⁰

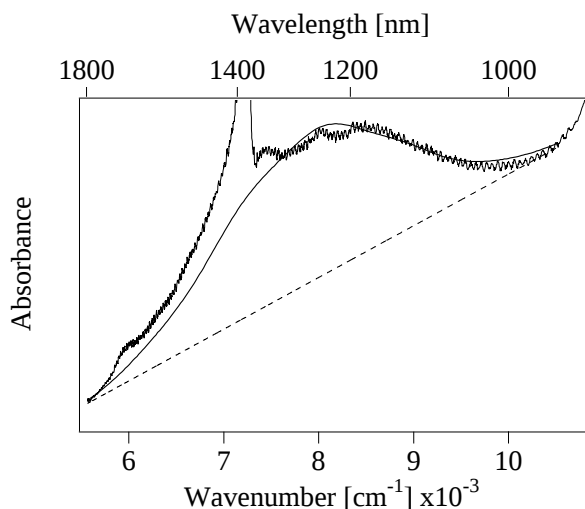


Figure 4. Intervalence charge transfer band of solid [Fe(II)Fe(III)BPMP(OPr)₂](BPh₄)₂, a localized mixed-valence compound.¹³ The spectrum was measured at 80 K (experimental: dotted line, calculation: solid line). The sharp absorption at 7000 cm⁻¹ is caused by the cryostat windows.

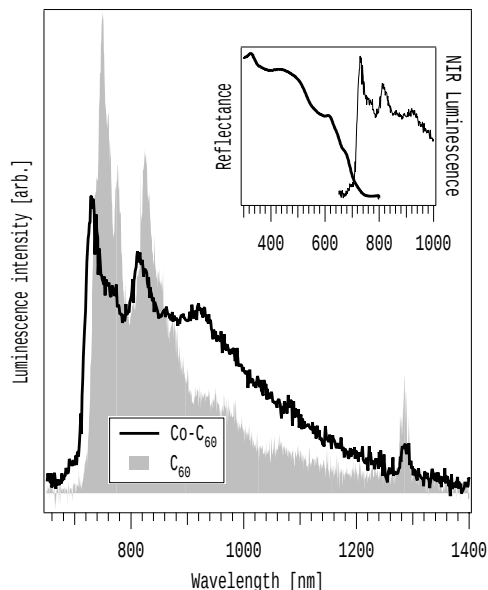


Figure 5. Luminescence spectrum of $\text{NaCoC}_{60}\cdot 3\text{THF}$ at 10 K. The luminescence spectrum of pure C_{60} is added for comparison (gray shading). The room temperature powder reflectance spectrum of $\text{NaCoC}_{60}\cdot 3\text{THF}$ is compared to the luminescence spectrum in the inset.

leads to higher energy (shorter wavelength) and to an enhancement of the vibronic intensity between 900 and 1100 nm.

The inset to Figure 5 illustrates that the high energy side of the NIR luminescence spectrum coincides with the onset of the absorption band which dominates the visible spectrum of these dark powders. The energy of the lowest electronic excited state is determined, by this comparison, to be $14,300\text{ cm}^{-1}$ for $\text{NaCoC}_{60}\cdot 3\text{THF}$. NIR spectroscopy is a powerful technique in the characterization of the chemical structure and the electronic states for this class of new materials.

Acknowledgement

This work was made possible by research grants from NSERC (Canada) and FCAR (Province of Quebec). U. Oetliker thanks the Swiss National Science foundation for a research fellowship. We acknowledge Professor M.C. Baird and D.K. Patel (Queen's University, Kingston, Ontario) for their gift of the $\text{C}_{60}\text{--Co}$ compounds.

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