

Metal-ligand bonding in six-coordinate d-block complexes probed by luminescence spectroscopy at variable pressure

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Abstract: Luminescence spectra measured at variable pressure can reveal unique insight on ground- and emitting state properties of transition metal compounds. This chapter summarizes illustrative results for chromium(III) complexes with the d^3 electron configuration and oxo complexes of rhenium(V) and molybdenum(IV) with the d^2 configuration. Their luminescence transitions only involve electronic configuration changes within the t_2 (O point group) molecular orbitals, leading to narrow spin-flip bands and broad bands with vibronic structure for the chromium(III) and metal-oxo complexes, respectively.

Keywords: luminescence spectroscopy, variable pressure, chromium(III) complexes, rhenium(V) complexes, molybdenum(IV) complexes, metal-oxo complexes

1. Introduction

Luminescence spectroscopy is one of the key techniques to advance our understanding of the electronic structure of many compounds and materials, with important applications ranging from molecular photochemistry to materials science and optical technology. Spectroscopic studies using variable pressure can provide additional insight on specific effects, even at the modest pressures of up to approximately 30 kbar discussed here [1]. Many luminescence processes involve only the transition from the lowest-energy excited state to the ground state, leading to relatively simple spectra without overlapping bands, therefore allowing the observation of weak, forbidden transitions.

Several reviews of luminescence properties of transition metal compounds and doped materials at high pressure have been published [2-7]. In contrast to these general reviews, we focus here on variable-pressure luminescence spectra of two specific categories of molecular complexes: First, spin-flip luminescence bands, recently reviewed in depth for six-coordinate d-block complexes [8], and second, luminescence spectra of metal-oxo complexes [9]. The first type of transition has been studied in great detail for many solids doped with chromium(III) ions [3], with ruby being the prototype and its spin-flip luminescence the prevalent standard for pressure calibration [10-13], as discussed in the chapter on diamond anvil cell techniques earlier in this volume. Isoelectronic molecular chromium(III) complexes show a much wider variety of variable-pressure luminescence properties, most importantly stronger shifts of the band maxima to longer wavelength than reported for the doped solids [3]. The variable-pressure luminescence spectra of metal-oxo complexes of rhenium(V) and molybdenum(IV) with the d^2 configuration represent the second category summarized in this chapter. Their luminescence maxima can shift to either longer or shorter wavelength, and this wide variation provides insight on well-established metal-ligand bonding concepts.

Both families of complexes discussed here are six-coordinate with only the t_2 (O point group) molecular orbitals populated in the ground and emitting states. In chromium(III) complexes, these orbitals are approximately degenerate, as illustrated in Figure 1. Both the ground and emitting states arise from the t_2^3 electron configuration. Intraconfigurational electronic transitions between the 4A_2 and 2E states do not cause structural changes and luminescence spectra with narrow overall bandshapes are observed. In contrast, the t_2 levels

are no longer degenerate in the metal-oxo compounds of D_4 point group symmetry, also schematically illustrated for *trans*-dioxo rhenium(V) complexes in Figure 1. The energy difference between these levels has been denoted as Δ_π , in formal analogy to the ligand-field splitting Δ_o , also shown in Figure 1. The luminescence transition in the metal-oxo complexes involves changes in electron populations along both the short metal-oxo bonds, oriented along the molecular z axis in Figure 1, and along the longer bonds to ancillary ligands in the x,y plane. As a consequence, spectra with broad bands are observed.

The luminescence spectra of both categories of molecular systems compared in the following formally involve only electronic states arising from the t_2 molecular orbitals, but the observed spectroscopic phenomena vary widely, providing an interesting comparison to illustrate the detailed insight that can be gained from variable-pressure luminescence spectroscopy.

[Insert Fig. 1 here.]

2. Variable-pressure spin-flip luminescence of molecular chromium(III) complexes

The red R-line luminescence of ruby is among the most studied spectroscopic transitions, used to probe many different physical processes and relevant as the first source of laser light [14]. The pressure-induced shift of the ruby R-lines, seminal spin-flip luminescence bands, has been studied over a wide range of pressures [10-13]. Such shifts for ruby and numerous other doped oxides are always to lower wavenumber (longer wavelength, red shift) and small, on the order of $-0.1 \text{ cm}^{-1}/\text{kbar}$ to $-1 \text{ cm}^{-1}/\text{kbar}$ [3]. This is schematically illustrated in Figure 2 and straightforward to understand, as both the 4A_2 ground state and the 2E emitting state arise from the same t_2^3 electron configuration and their energies are therefore almost parallel in Figure 2, similar to a conventional Tanabe-Sugano diagram with the ligand field strength Δ_o on the horizontal axis. All spin-flip transitions are represented by parallel ground and emitting states in such diagrams [8]. No population change of orbitals with varying bonding characteristics occurs in these transitions, leading to very small changes of the transition energy caused by decreases of the Racah parameters B and C, a consequence of the bond compressions induced by pressure.

In contrast, significant shifts to higher wavenumber (shorter wavelength, blue shift) are observed for the interconfigurational transition involving the 4T_2 excited state, observable in absorption spectra and for some systems also as luminescence bands. These shifts range from $+10\text{ cm}^{-1}/\text{kbar}$ to $+30\text{ cm}^{-1}/\text{kbar}$ [3], absolute values higher by an order of magnitude than for the spin-flip transitions of ruby and other doped solids. Figure 2 schematically shows this stronger blue shift for the 4T_2 excited state, again qualitatively similar to a Tanabe Sugano diagram for the d^3 configuration. Pressure-induced metal-ligand bond length decreases lead to a strong destabilization of the σ antibonding (σ^*) e orbitals and therefore to a higher ligand field splitting Δ_o . This is the most important factor defining observed maxima for interconfigurational transitions involving a population change in the e levels. Reported values are similar in magnitude for numerous doped solids and molecular compounds [3,15]. The effect of pressure on the t_2 levels is smaller and can not be unambiguously identified from shifts of the 4T_2 band for chromium(III) complexes with O point group symmetry.

[Insert Fig. 2 here.]

Only a handful of molecular chromium(III) complexes have been studied by variable-pressure luminescence spectroscopy, due to their low quantum yields under ambient conditions are often extremely low, both in solution and for solid samples. Recent developments in synthetic chemistry have led to optimized ligand designs in order to overcome this limitation [16-18]. Representative luminescence spectra of such a complex in solution and in the solid state are shown in Figure 3 [19]. This $[\text{Cr}(\text{ddpd})_2]^{3+}$ complex has been named molecular ruby and is six-coordinate with two expanded terpyridine-type N,N'-dimethyl-N,N'-dipyridine-2-yl-pyridine-2,6-diamine (ddpd) ligands, resulting in a nearly perfect octahedral coordination geometry. The strong-field ddpd ligands cause a very high energy difference between the 2E and 4T_2 excited states, an important factor contributing to the intense luminescence observed at ambient conditions.

[Insert Fig. 3 here.]

The luminescence of molecular ruby occurs at longer wavelength than the ruby R-lines and spectra measured at variable pressure are similar in solution and in the solid state, indicative of an absence of intermolecular effects, for example due to hydrogen bonding [20]. Transitions from both the 2E and the thermally populated 2T_1 states are observed. The luminescence maxima in Figure 3 show a strong red shift with increasing pressure, on the order of $-15\text{ cm}^{-1}/\text{kbar}$, a trend also illustrated in Figure 2. The absolute value of this shift is therefore comparable in magnitude, but different in sign, to the effect of pressure on interconfigurational transitions, such as those involving the 4T_2 state in Figure 2. This is a surprising observation and shows that variable-pressure luminescence spectroscopy can reveal properties beyond the expectations based on qualitative transition assignments and electron configurations of the ground and emitting states. Variable-pressure luminescence spectroscopy shows that the electronic structure of the emitting state is distinctly different from the ground state, even for spin-flip transitions as illustrated by the spectra in Figure 3.

We rationalize this strong shift as a combination of several effects: a first contribution is the decrease of the Racah parameters, a second contribution are structural distortions, leading to a split 2E state and a lower-energy emitting state, and finally vibronic effects involving the extended electronic system of the tridentate ligands can also contribute to the sizeable red shift. All three effects are beyond a traditional Tanabe-Sugano diagram, and the strong red shift measured for molecular ruby in Figure 3 can not be rationalized in terms of a simple increase of the ligand field strength Δ_o . The second and third effects are negligible in doped ionic solids and probably small for molecular complexes with simple ligands, leading to lower absolute values of the pressure-induced shifts. The spectra in Figure 3 show therefore a unique aspect of variable-pressure luminescence from modern molecular chromium(III) complexes. Table 1 shows that pressure-induced red shifts of spin-flip luminescence bands for molecular complexes are generally stronger in absolute value than for ruby, with molecular ruby in Figure 3 showing the strongest red shift reported to date for chromium(III) complexes.

Even stronger pressure-induced red shifts might be observed for chromium(III) complexes with longer wavelength near-infrared luminescence. Luminescence spectra of two such

complexes have recently been reported [21,22]. It is for such molecular systems that variable-pressure luminescence spectroscopy can provide useful complementary information and insight.

[Insert Table 1 here]

3. Variable-pressure luminescence of metal-oxo complexes with the d^2 configuration

The second family of d-block metal complexes discussed in this chapter is also six-coordinate, but with distinctly different bonds along one axis due to short metal-oxo multiple bonds [9]. The oxo complexes of rhenium(V) and molybdenum(IV) compared here both have the d^2 electron configuration, leading to singlet and triplet electronic states [9]. The difference between the short, multiple metal-oxo bonds along the molecular z axis defined in Figure 1 and the longer, weaker bonds to ancillary ligands in the x,y equatorial plane lifts the degeneracy of the t_2 orbitals (O point group) and the effect is sufficient in size to lead to a singlet ground state with the electrons paired in the lower energy b_2 (d_{xy}) orbital (D_4 point group) [30-33]. The lowest energy excited state is a triplet, with one electron occupying the higher-energy e orbitals with π^* metal-oxo character. The energy difference between these states leads to luminescence in the orange-red wavelength range. The bonding characteristics of the b_2 orbital can be either π^* for donor ligands or π for acceptor ligands. The resulting pressure-induced energy variations are distinctly different from the Tanabe-Sugano diagram for the d^2 configuration in the O point group.

[Insert Fig. 4 here.]

Figure 4 schematically illustrates the pressure-induced energy difference between the ground and emitting states, with the energy of the 3E emitting state held constant, analogous to the 4A_2 ground state in Figure 2, allowing to visualize the qualitative effects of pressure on the luminescence band maximum for metal-oxo complexes. The diagram is based on the qualitative assumption that the metal-oxo multiple bonds are less compressed than the

metal-ligand single bonds in the equatorial plane, and it is therefore the pressure effect on the b_2 orbitals that defines the shift of the luminescence maxima. The effect of pressure on the ground state energy depends on the type of π bonding with the ligands in the equatorial plane: for π donor ligands, the b_2 level is antibonding (π^*) and a destabilization occurs as bond lengths shorten; in contrast, a stabilization is expected for π acceptor ligands, where the b_2 level is π bonding. This difference leads to pressure-induced shifts of luminescence maxima with different signs, as shown in Figure 4, likely one of the clearest experimental distinctions between π donor and π acceptor ligands. Figures 5 and 6 show experimental spectra documenting this difference.

[Insert Fig. 5 here.]

The luminescence spectra for these metal-oxo complexes are broad bands, due to vibronic progressions involving metal-ligand vibrational modes [30,31,33]. The strongest vibronic progression involves metal-oxo stretching modes with frequencies on the order of 900 cm^{-1} , leading to the resolved maxima in Figure 5 [34]. The spectra in Figure 5 clearly show a pressure-induced red shift of the luminescence maximum, easily seen from the dotted lines connecting the two most intense vibronic peaks. Such red shifts are observed for many similar complexes with a variety of nitrogen donor ligands [35,36], as summarized in Table 2.

[Insert Fig. 6 here.]

The variable-pressure luminescence spectra of an isoelectronic molybdenum(IV) oxo complex with π acceptor ligands are shown in Figure 6 [37]. The band maxima show a clear blue shift between ambient pressure and 29 kbar, as indicated by the dotted line. The observed shifts in Figures 5 and 6 therefore correspond to the qualitative expectations from Figure 4. The values in Table 2 document that it is indeed possible to change the sign of the pressure-induced shift of the luminescence maximum through the type of ligands

coordinated in the equatorial plane, illustrating the detailed insight that can be gained from luminescence spectra measured at variable pressure.

[Insert Table 2 here]

4. Conclusions

The comparison of two categories of luminophores with related electron configurations illustrates the insight that can be gained from variable-pressure luminescence spectroscopy. Shifts of luminescence bands reveal detailed information on metal-ligand bonding and emitting-state properties. The recent discoveries of many new luminescent molecular compounds make such experiments even more useful in the future.

Acknowledgements

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Table 1: Pressure-induced shifts $\Delta E/\Delta P$ of spin-flip luminescence maxima E_{\max} for chromium(III) compounds.

Type	Compound	E_{\max} (cm ⁻¹)	$\Delta E/\Delta P$ (cm ⁻¹ /kbar)	References
Doped solids	Al ₂ O ₃ :Cr ³⁺ (Ruby)	14404	-0.75 to -0.77	[10,11,13]
Molecular Complexes	[Cr(NH ₃) ₆](NO ₃) ₃	15225	-4	[23]
	{rhodo}Cl ₅ ·H ₂ O‡	~14585	-5.6 ± 0.6	[24,25]
		~14680	-4.8 ± 0.4	
		~14165[14 K]†	-4.2 ± 0.4	
	{triol}(ClO ₄) ₃ ‡	~14165	-8.1 ± 0.5	[24,25]
		~14475	-5.4 ± 0.3	
		~14595[14 K]†	-4.1 ± 0.2	
	[Cr(urea) ₆](ClO ₄) ₃	14191 [1.3 K]	-5.4 ± 0.5	[26]
	[Cr(urea) ₆]I ₃	-	-3.1 ± 0.5	[26]
	[CrF ₆](NH ₄) ₃	15583†	-7.8 [>88 kbar]	[27]
	[NaCr(ox) ₃][Ru(bpy) ₃]	~14380	-2.5 ± 1.2	[28]
	[Rh(bpy) ₃][NaCr(ox) ₃]ClO ₄	~14380	-2.6	[28]
	[Cr(bpy) ₃][NaRh(ox) ₃][ClO ₄]	~13714	-6.1	[29]
	[Cr(bpy) ₃][NaAl(ox) ₃][ClO ₄]	~13685	-7.9	[29]
	[Cr(H ₂ tpda) ₂][ClO ₄] ₃	12761	-13.0	[19]
	[Cr(ddpd) ₂][PF ₆] ₃	12872	-13.0	[19]
	[Cr(ddpd) ₂][BF ₄] ₃	12876	-14.5	[19]

Abbreviations: {rhodo}: [(NH₃)₅Cr(μ-OH)Cr(NH₃)₅]⁵⁺, {triol}: tris-(μ-hydroxo)-bis-[(1,4,7-trimethyl-1,4,7-triazacyclononane) chromium(III)]³⁺, ox: oxalate, bpy: 2,2'-bipyridine, H₂tpda: 2,6-bis(2-pyridylamino)pyridine, ddpd: N,N'-dimethyl-N,N'-dipyridine-2-yl-pyridine-2,6-diamine. † Not observed under ambient conditions; position has been extrapolated from measurements at higher pressure. ‡ Bimetallic complexes with exchange coupling, resulting in multiple electronic origins.

Table 2: Pressure-induced shifts $\Delta E/\Delta P$ of luminescence maxima E_{\max} for metal-oxo compounds of rhenium(V) and molybdenum(IV).

Compound	E_{\max} (cm⁻¹)	$\Delta E/\Delta P$ (cm⁻¹/kbar)	References
<i>trans</i> -[ReO ₂ (tmen) ₂]Cl	15590	-4.6	[34]
<i>trans</i> -[ReO ₂ (pyridine) ₄]I	15360	-15.7	[36]
<i>trans</i> -[ReO ₂ (en) ₂]Cl	13780	-6.8	[35]
[MoOF(pyridine) ₄]BPh ₄	13000	-7.5	[37]
[MoOCl(CN- <i>t</i> -Bu) ₄]BPh ₄	11950	+12.0	[37]

Abbreviations: tmen: tetramethylethylenediamine, en: ethylenediamine

Figure captions

Figure 1: Schematic structures of complexes compared in this chapter with ground and emitting state assignments and relevant molecular orbital energy levels in O and D_4 point group symmetry.

Figure 2: Schematic pressure-induced energy variations for luminescent states of chromium(III) complexes. The 2E initial state for spin-flip luminescence is denoted by solid and dotted lines for molecular chromium(III) complexes and ruby, respectively. The 4T_2 emitting state of some chromium(III) compounds is shown for comparison. The 4A_2 ground-state energy is defined by a horizontal line. $t_2^n e^m$ (O point group) electron configurations are given for all electronic states shown.

Figure 3: Variable-pressure luminescence spectra of molecular ruby, $[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$, at room temperature in the solid state (a) and in aqueous solution (b). Copyright Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim © 2018 [19] – reprinted with permission.

Figure 4: Schematic pressure-induced energy variations for luminescence transitions of metal-oxo compounds with the d^2 electron configuration. Solid and dotted vertical arrows correspond to luminescence maxima E_{max} for complexes with π donor and π acceptor ligands in the equatorial plane perpendicular to the metal-oxo bonds. Vertical arrows at low and high pressure illustrate the different signs of pressure-induced shifts defined by metal-ligand bonding characteristics. The 3E emitting-state energy is shown as a horizontal line in this representation. The 1A_1 ground state is denoted by solid and dotted lines for π donor and π acceptor ligands, respectively. $b_2^n e^m$ (D_4 point group) electron configurations are given for all electronic states shown.

Figure 5: Variable-pressure luminescence spectra of *trans*- $[\text{ReO}_2(\text{tmen})_2]\text{Cl}$ (tmen: tetramethylethylenediamine). The pressure-induced red shifts of the two most intense vibronic maxima are represented by the dotted lines, as schematically illustrated by the solid arrows in Figure 4.

Figure 6: Variable-pressure luminescence spectra of $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4][\text{BPh}_4]$. The dotted line is a guide for the eye to show the blue shift of the luminescence maximum with increasing pressure, as schematically illustrated by the dotted arrows in Figure 4.

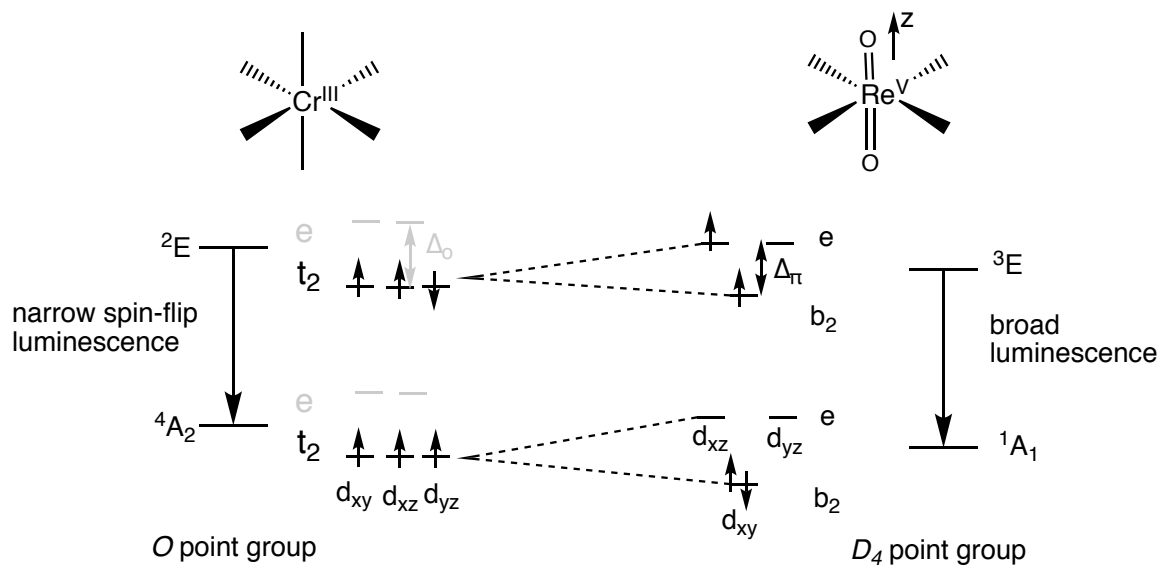


Figure 1

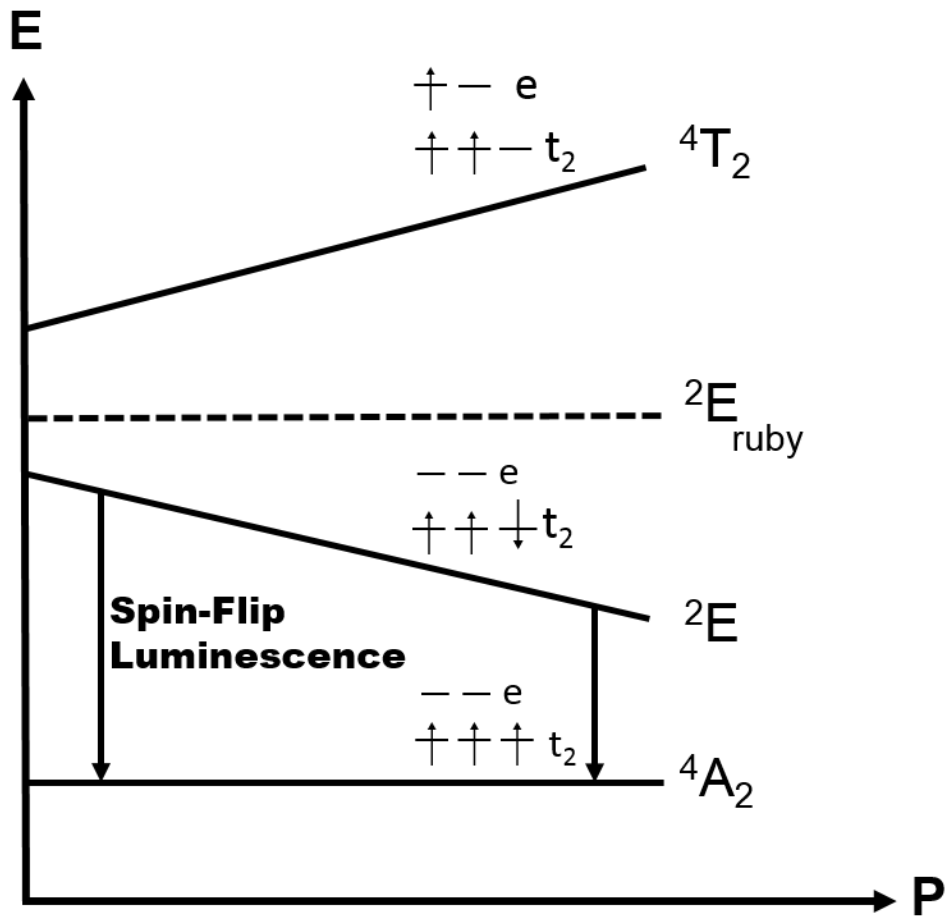


Figure 2

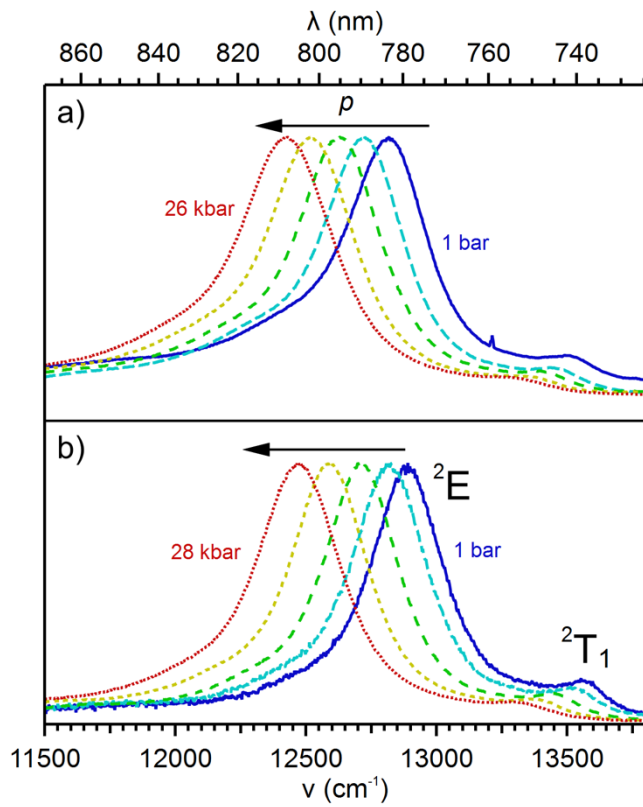


Figure 3

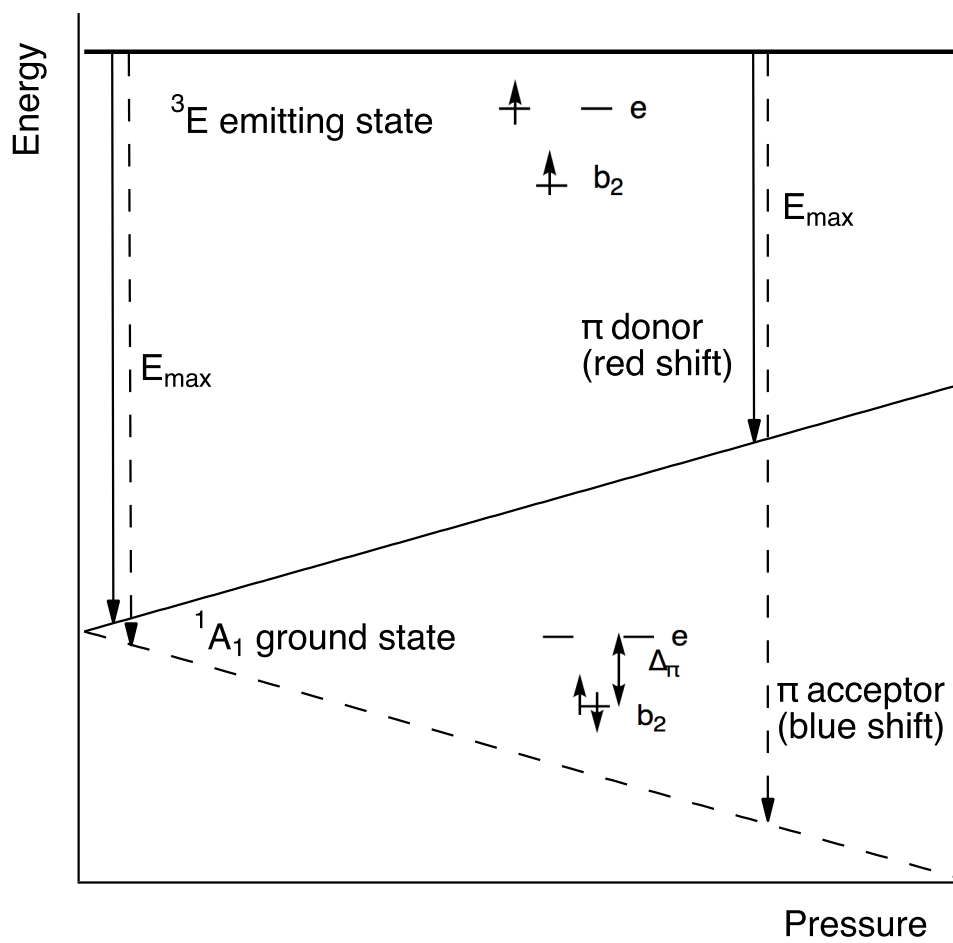


Figure 4

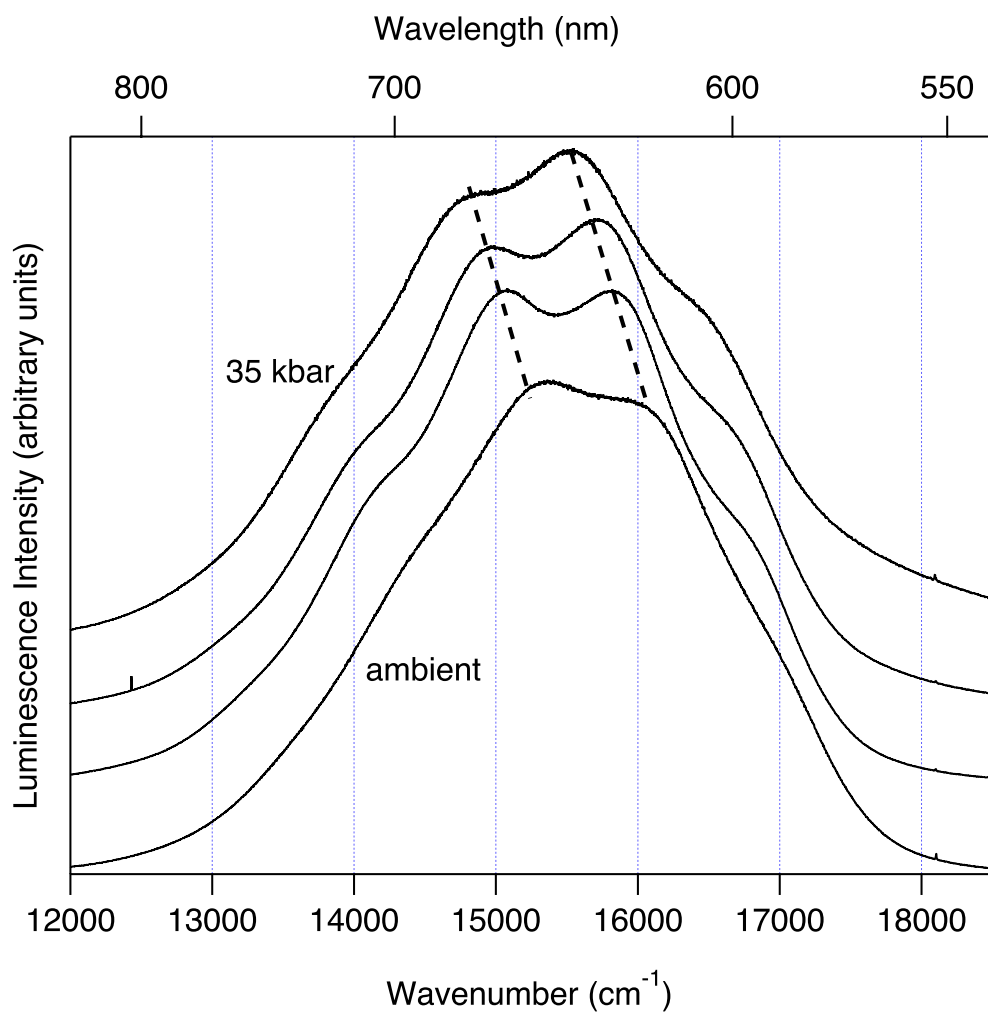


Figure 5

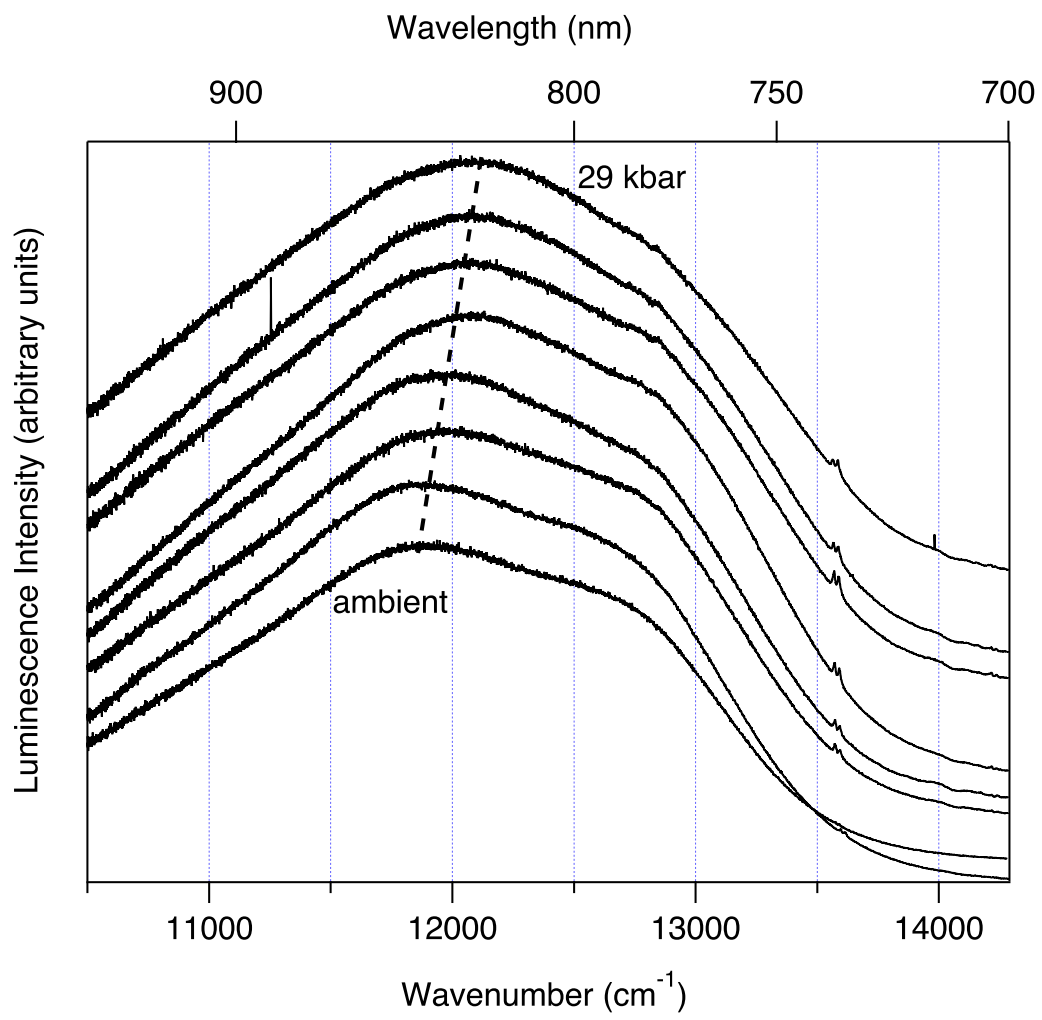


Figure 6